I

THE HYDRATION OF CROTONALDEHYDE

II

THE COORDINATION OF SILVER ION WITH UNSATURATED MOLECULES

III

STEREOCHEMICAL RELATIONSHIPS IN THE CONVERSION OF ACETATES TO BROMIDES

Thesis by
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To My Wife

- ABSTRACT -

I. The hydration of crotonaldehyde and the dehydration of aldol in dilute aqueous solutions of acids are first order with respect to the organic compound and to the acid. Energies of activation for hydration and dehydration are 18.23 and 24.48 kcal., respectively. Equilibrium is reached when 47% of the crotonaldehyde has been converted to aldol at 25° and 39% at 35°.

II. Complex formation between silver ion and a variety of unsaturated molecules in aqueous solution has been studied and equilibrium constants for the reactions of formation of several kinds of complex ions have been determined. A structure is proposed for the olefin-silver ion complex, and trends in equilibrium constants are explained in terms of steric and resonance effects.

III. The occurrence of an odd number of inversions in the transformation of 2,3-diacetoxybutane to 2,3-dibrombutane has been confirmed. 1,2-Diacetoxycyclohexane fails to give 1,2-dibromcyclohexane on treatment with aqueous fuming hydrobromic acid. 2-Acetoxyoctane on treatment with fuming hydrobromic acid gives a bromide of preponderantly inverted configuration, but the retention of optical purity is only 67%.

I

THE HYDRATION OF CROTONALDEHYDE

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 599]

The Hydration of Unsaturated Compounds. VI. The Rate of Hydration of *trans*-Crotonaldehyde. The Equilibrium between *trans*-Crotonaldehyde and Aldol in Dilute Aqueous Solution[1]

BY SAUL WINSTEIN AND HOWARD J. LUCAS

The conversion of crotonaldehyde to aldol and the more important reverse reaction are well known. Wurtz[2] found that crotonaldehyde in hydrochloric acid solution was transformed to aldol. Numerous methods for the production of crotonaldehyde are based upon the thermal decomposition of aldol, with or without the addition of a catalyst.[3] Although it is evident that an equilibrium is involved in the aldol–crotonaldehyde system, apparently not even approximate data on the equilibrium constant appear in the literature.

Continuing the work on the hydration of unsaturated compounds and extending it to compounds other than hydrocarbons, we have investigated the kinetics of the hydration of crotonaldehyde in dilute aqueous solutions of nitric and perchloric acids.

Materials.—The *trans*-crotonaldehyde[4] was Niacet material twice distilled through a 100-cm. column of glass rings. The middle fraction, b. p. 101.8–102.0° at 744 mm., purity 99.1% by bromine absorption, was used for the hydrations.

Analysis.—The analysis for crotonaldehyde was carried out similarly to the isobutene analysis[5] except that the vacuum technique was unnecessary, an ordinary iodine titration flask being used. The acid was added last and the titration flask could be stoppered before any bromine was liberated from the bromate–bromide solution. In general, there was no variation of results with time of bromination, for analyses in which the crotonaldehyde and the bromine (100% excess) remained together for lengths of time varying from five to thirty minutes yielded results all agreeing within 0.2%.

However, analyses of solutions near equilibrium, *i. e.*, those containing considerable amounts of aldol, did vary with time, more bromine being consumed at longer times. The variation was small, indicating a possible absolute error of 0.3%, in the percentage conversion of the crotonaldehyde. This error was eliminated by using only a small excess of bromate–bromide solution, *i. e.*, an amount equivalent to about 2 ml. of 0.02 *N* thiosulfate. The crotonaldehyde could be accurately and quantitatively determined by brominating for five minutes with this slight excess of bromate, even when acetaldehyde, which it was feared might possibly develop in the solutions, had been added in amounts equivalent to the crotonaldehyde present.

Method.—A crotonaldehyde solution was made up, brought to temperature, and analyzed. Aliquot portions were pipetted into volumetric flasks, diluted almost to volume, proper amounts of nitric or perchloric acids were added, and the volume was adjusted quickly to the final value. The solutions were then kept in glass-stoppered flasks in a thermostat at either 25.0 ± 0.05° or 35.0 ± 0.05°. All the operations were done at constant temperature. Time was counted from the time of the addition of the acid. The initial concentration of crotonaldehyde was known from the analysis of the original stock solution. At suitable times samples were withdrawn and analyzed for crotonaldehyde. The acid concentration of the final solution was determined by titration with standard alkali. In the first runs with nitric acid, the titration with standard base was carried out at the beginning and the end of an experiment. The analyses agreed to within experimental error. No reduction products of nitric acid could be detected.

Stability of Solutions.—Without the addition of acid, aqueous solutions of crotonaldehyde are quite stable. Thus at concentrations of 0.02 and 0.03 *M*, crotonaldehyde at 25° in glass-stoppered bottles showed a decrease of unsaturation of approximately 0.3% in seventy-five hours and the development of acidity corresponding to the oxidation of about 2% of the aldehyde in one month, due to a slow oxidation by traces of oxygen. At 35°, the decrease in unsaturation was only 0.2% during the time that elapsed in a hydration experiment, while oxidation was only 0.5% in seventy-five hours.

Course of Hydration.—When aqueous crotonaldehyde solutions were made acid at 25°, the unsaturation of the solutions decreased relatively rapidly to approximately one-half the original value and then very slowly "drifted" downward, indicating a relatively rapid approach to equilibrium, accompanied by a slow drift. Although somewhat troublesome, this drift was not rapid enough to be very serious.

The drift could have been due to several causes. Ingold[6] found the equilibrium between aldol and acetaldehyde in potassium carbonate solution was completely displaced toward aldol. The solutions were concentrated in aldol. In the present case the solutions were dilute, favoring a slow partial dissociation of the aldol. The odor of acetaldehyde could be detected in the hydrating crotonaldehyde solutions that had stood for some time.

Slow removal of material by further aldol condensations

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(1) For the preceding paper of this series see THIS JOURNAL, **59**, 722 (1937).

(2) Wurtz, *Bull. soc. chim.*, [2] **42**, 286 (1884).

(3) Wurtz, *Compt. rend.*, **87**, 45 (1878); Usines de Melle, German Patent 598,015 (1934); Maude, U. S. Patent 1,738,659 (1929).

(4) Young, THIS JOURNAL, **54**, 2498 (1932).

(5) Lucas and Eberz, *ibid.*, **56**, 460 (1934).

(6) E. H. Ingold, *J. Chem. Soc.*, **125**, 435 (1924).

even at the low concentrations used is also a possible factor contributing to the drift. It is also conceivable that a very small fraction of α-hydroxybutyraldehyde is formed by an irreversible hydration of the crotonaldehyde, giving rise to a slow gradual decrease in the unsaturation of the solution.

Data and Discussion.—When solutions of crotonaldehyde, 0.032, 0.016, and 0.008 *M*, respectively, were made 0.5 *N* in nitric acid, and C_0/C_t (C_0 and C_t being initial and time values of the unsaturation) plotted against the time, *t*, the points for the three solutions fell on the same smooth curve for the first portion of the hydration. This indicated that the rate of hydration is first order with respect to crotonaldehyde and that side reactions of a higher order with respect to crotonaldehyde are negligible. It was possible to obtain values for the specific reaction rate, k_1, by determining initial slopes, but an analytical method was considered better.

Considering the reaction symbolized by equation (1)

$$H_2O + C_4H_6O \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_4H_8O_2 \qquad (1)$$

here k_1 and k_2 are the specific reaction rate constants for the forward and back reactions, respectively, then the integrated expression for the approach to equilibrium, starting with crotonaldehyde, is shown in equation (2) for the case where

$$2.303 \log \epsilon/(\epsilon - x) = (k_1 + k_2)t \qquad (2)$$

the forward and back reactions are first order with respect to crotonaldehyde and aldol, respectively. In the above expression, ϵ represents the fraction of original crotonaldehyde converted to aldol at equilibrium and x denotes the fraction converted at time t.

In treating the data of any run, ϵ was varied so as to give the best constancy of $[\log \epsilon/(\epsilon - x)]/t$ neglecting the long time points where the slow drift had affected considerably the values of x.

The data for two typical runs are shown in Tables I and II. The constancy of $[\log \epsilon/(\epsilon - x)]/t$ indicates that the approach to equilibrium follows the unimolecular law. The values for k_1 and k_2 shown were calculated by means of equations (3) and (4)

$$k_1 = \epsilon(k_1 + k_2) \qquad (3)$$
$$k_2 = (1 - \epsilon)(k_1 + k_2) \qquad (4)$$

It is to be emphasized that the values of k_1 are more accurate than those of k_2, since k_1 is less sensitive to a change in ϵ. The accuracy with which the experimental data were fitted is shown by a comparison between the experimental values of x and those calculated from the chosen ϵ and the derived average $(k_1 + k_2)$. The agreement is within experimental error nearly to equilibrium, but at the larger values of t, the agreement is not so good, due to the drift. The order of magnitude of the drift can be seen from the difference in the experimental and calculated values of x, Tables I and II.

TABLE I

HYDRATION OF CROTONALDEHYDE AT 25° IN 1.905 *N* NITRIC ACID

$\epsilon = 0.442$

Time, hrs.	100 x		Log	$\frac{\log \epsilon/(\epsilon - x)}{t}$
	Exptl.	Calcd.	$\epsilon/(\epsilon - x)$	
2.13	8.8	8.7	0.0959	0.0450
4.17	15.3	15.4	.1838	.0441
6.30	21.0	21.0	.2794	.0443
12.60	31.7	32.0	.5488	.0436
23.48	40.3	40.2	1.054	.0448
52.98	46.1	44.0		
100	48.7	44.2		

Mean 0.0444

Per cent. mean deviation 1.0

$k_1 + k_2$ 0.1022 hrs.$^{-1}$

k_1 .0452

k_2 .0570

TABLE II

HYDRATION OF CROTONALDEHYDE AT 35° IN 1.806 *N* NITRIC ACID

$\epsilon = 0.378$

Time, hrs.	100 x		Log	$\frac{\log \epsilon/(\epsilon - x)}{t}$
	Exptl.	Calcd.	$\epsilon/(\epsilon - x)$	
0.41	4.3	4.3	0.0523	0.127
.79	7.8	7.8	.1000	.127
1.22	11.6	11.6	.1593	.130
1.73	15.7	15.3	.2327	.134
2.41	19.6	19.5	.3179	.132
4.04	26.8	26.6	.5359	.132
7.67	34.1	34.0	1.009	.132
24.43	39.6	37.8		

Mean 0.1306

Per cent. mean deviation 1.7

$k_1 + k_2$ 0.300 hrs.$^{-1}$

k_1 .114

k_2 .186

The monomolecular approach to equilibrium for runs covering a range of acid concentrations is shown in Figs. 1 and 2, where $\log \epsilon/(\epsilon - x)$ (ϵ varying slightly in the different runs) is plotted against time.

Table III is a summary of the results of the runs carried to equilibrium. In the runs where μ, the ionic strength, is different from the acid concentration, potassium nitrate was added in amount equal to the difference. $k_1/(H_3O^+)$ and $k_2/(H_3O^+)$ signify the ratio of the specific reaction rate constants, k_1 and k_2, to the acid concentration. The values of k_1, Table III, agree well with the values of k_1 obtained by the method of initial slopes. The mean deviation between the two sets of values in eleven cases was 2.2%

The approximate constancy of $k_1/(H_3O^+)$ and $k_2/(H_3O^+)$ at any one temperature indicates a first order dependence of both the hydration and the dehydration reactions upon the acidity. Therefore, after replacing equation (1) by equation (5)

$$C_4H_6O + H_3O^+ \rightleftarrows C_4H_8O_2 + H^+ \quad (5)$$

k_1, in agreement with the Brönsted theory, is expressed by equation (6), after canceling activity coefficients of two positively charged ions

$$k_1 = k_0\,(H_3O^+)\gamma \qquad (6)$$

Here k_0 is the specific rate constant of hydration adjusted to 1 *N* acid, and γ is the activity coefficient of crotonaldehyde.

The Salt Effect.—Inspection of Table III discloses that with no added salt (Expts. 5 to 17) $k_1/(H_3O^+)$ is constant to several per cent. over the range of acid concentration, in general increasing as the acid concentration decreased. Thus, as the ionic strength increases, $k_1/(H_3O^+)$ decreases, apparently in contradiction to expectations from equation (6). However, comparison of run 4 with 5 or of 3 with 6 discloses that increase of ionic strength by addition of potassium nitrate does increase $k_1/(H_3O^+)$, the increase being of the order of magnitude of the salting out effect one would estimate. Considering runs 1 to 4, it is evident that at constant ionic strength, $k_1/(H_3O^+)$ increases by some 14% as the acid concentration decreases from 2 to 0.5 *N*, the potassium nitrate concentration increasing. These things point to the non-equivalence of the salt effects of nitric acid and potassium nitrate. Since, in the case of isobutene,[5] $k_1/(H_3O^+)$ was constant up to 1 *N* nitric acid, while in this work k_1 is reliable to 2 or 3%, the trends mentioned above deserve notice. Also, in general, ϵ exhibits a trend with acid concentration of the same order of magnitude as the drift in $k_1/(H_3O^+)$ at constant ionic strength. Thus, $k_2/(H_3O^+)$, although somewhat erratic, is constant at constant ionic strength (Expts. 1 to 4) and varies with a change in the ionic strength, increasing as the ionic strength increases. This is the behavior one would expect.

This can be explained by a "salting in" of the crotonaldehyde by acid, according to a reaction such as is shown in equation (7)

$$C_4H_6O + H_3O^+ \rightleftarrows C_4H_6O{\cdot}H^+ + H_2O \qquad (7)$$

the crotonaldehyde competing with H_2O for the proton somewhat successfully. Thus, as the acid concentration increases, this reaction more than neutralizes the effect of increase of ionic strength. This would explain the trends in $k_1/(H_3O^+)$ and in ϵ, if it can be said that the similar reaction of aldol takes place to a much smaller extent.

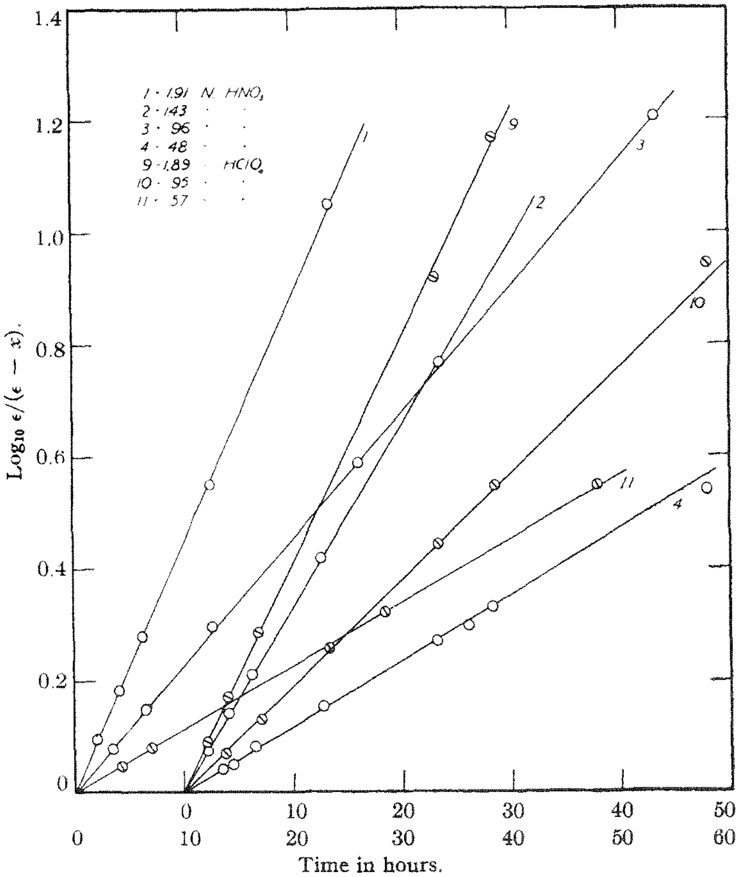

Fig. 1.—Plot of $\log_{10} \epsilon/(\epsilon - x)$ against *t* for the hydration of crotonaldehyde at 25°.

A comparison of nitric and perchloric acids shows that rate constants are 6 or 7% lower for the latter than for the former at both temperatures. It is interesting that in the case of the hydrocarbons trimethylethylene[7] and ethyl-

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[7] Lucas and Liu, THIS JOURNAL, **56**, 2138 (1934).

TABLE III

DATA ON THE HYDRATION OF CROTONALDEHYDE AT 25°

No.	Acid	Acid, N	μ	C_0, M	ϵ	$k_1 + k_2$, hrs.$^{-1}$	k_1, hrs.$^{-1}$	k_2, hrs.$^{-1}$	$\frac{k_1}{(H_3O^+)}$, hrs.$^{-1}$	$\frac{k_2}{(H_3O^+)}$, hrs.$^{-1}$
1	HNO_3	1.905	1.90	0.032	0.442	0.1022	0.0452	0.0570	0.0238	0.0298
2	HNO_3	1.432	1.93	.032	.456	.0766	.0350	.0416	.0244	.0291
3	HNO_3	0.9564	1.96	.032	.466	.0523	.0244	.0279	.0255	.0292
4	HNO_3	.4784	1.98	.032	.480	.0270	.0130	.0140	.0272	.0292
5	HNO_3	0.5008	0.50	0.032	0.490	0.0247	0.0121	0.0126	0.0242	0.0252
6	HNO_3	1.004	1.00	.032	.485	.0490	.0238	.0252	.0237	.0251
7	HNO_3	0.5016	0.50	.016	.480	.0254	.0122	.0132	.0243	.0263
8	HNO_3	1.005	1.00	.016	.470	.0511	.0240	.0271	.0239	.0270
							Mean	(including 1)	.0240	.0267
9	$HClO_4$	1.886	1.89	0.032	0.440	0.0933	0.0410	0.0523	0.0217	0.0277
10	$HClO_4$	0.9493	0.95	.032	.482	.0440	.0212	.0228	.0223	.0241
11	$HClO_4$	.5697	.57	.032	.497	.0259	.0129	.0130	.0227	.0229
								Mean	.0222	.0249
					At 35°					
12	HNO_3	1.806	1.81	0.032	0.378	0.300	0.114	0.186	0.0632	0.103
13	HNO_3	0.9614	0.96	.032	.390	.1608	.0627	.0981	.0652	.102
14	HNO_3	.4826	.48	.032	.400	.0790	.0316	.0474	.0655	.098
								Mean	.0646	.101
15	$HClO_4$	1.872	1.87	0.032	0.360	0.307	0.111	0.196	0.0593	0.104
16	$HClO_4$	0.7502	0.75	.032	.400	.1131	.0452	.0679	.0602	.091
17	$HClO_4$	.3736	.37	.032	.410	.0564	.0231	.0333	.0618	.089
								Mean	.0604	.095

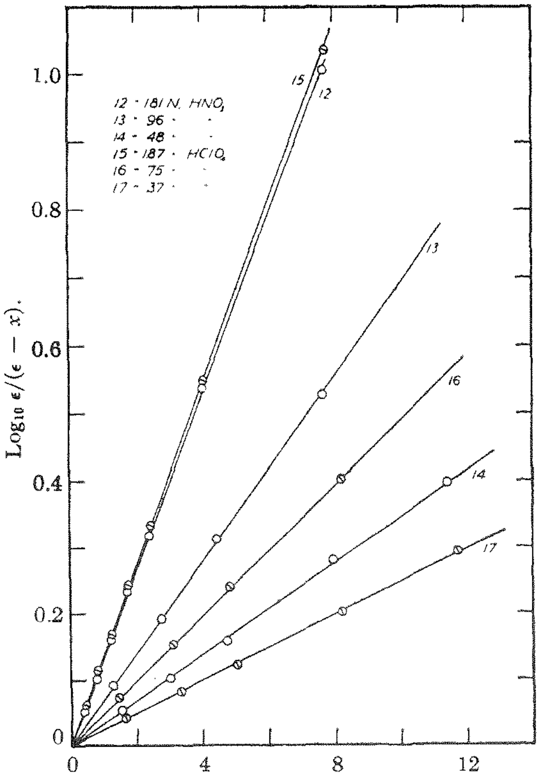

Fig. 2.—Plot of $\log_{10} \epsilon/(\epsilon - x)$ against t for the hydration of crotonaldehyde at 35°.

methylethylene,[8] nitric acid gave lower rates by 5 or 10%.

Temperature Coefficients and Activation Energies.—Table IV gives the temperature coefficients for the forward and back reactions at several approximate concentrations (N) of the two acids, the activation energies of the forward and back reactions (E_1 and E_2, respectively) and the difference ($E_2 - E_1 = -\Delta H$) between these values. The values other than the first set are quite consistent, for the mean deviation in the ΔH value of -6.25 kcal. per mole (excluding the starred value) is only 0.20 kcal. The heat of activation, E_1, of 18.2 kcal. for the hydration is

TABLE IV

TEMPERATURE COEFFICIENTS AND ACTIVATION ENERGIES OF HYDRATION, E_1, AND DEHYDRATION, E_2

Acid	N	$\frac{k_{1\ 35}}{k_{1\ 25}}$	$\frac{k_{2\ 35}}{k_{2\ 25}}$	E_1, kcal.	E_2, kcal.	$-\Delta H$ $E_2 - E_1$, kcal.
HNO_3	1.9	2.65	3.46	17.80	22.60	4.80*
HNO_3	0.95	2.74	3.92	18.40	24.90	6.50
HNO_3	0.5	2.70	3.80	18.10	24.40	6.30
$HClO_4$	1.9	2.73	3.76	18.30	24.20	5.90
$HClO_4$	0.85	2.70	3.77	18.10	24.20	6.10
$HClO_4$	0.47	2.72	3.88	18.25	24.70	6.45
Mean		2.72	3.83	18.23	24.48	6.25

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(8) Liu and Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

lower than the values for the hydrocarbons, 23.39 for isobutene,[5] 21.04 for methylethylethylene[8] and 18.92 for trimethylethylene.[7] Nevertheless, crotonaldehyde hydrates at a much lower rate, which at 25° is about 1% of that for isobutene. For isobutene ΔH of hydration is -11.56 kcal. per mole.[9] The difference in the values for isobutene and crotonaldehyde can be ascribed perhaps to conjugation energy in the case of crotonaldehyde.

Estimation of Drift Effect.—In order to obtain an estimate of the possible error introduced by the method of treating the data, rate expressions were set up for the cases where the drift was assumed to be due either to a first order disappearance of crotonaldehyde, specific reaction constant being k_3, or to a first order disappearance of aldol, reaction rate constant k_4. The resulting expressions for x as functions of the time are shown in equations (8) and (9)

$$x = 1 + \frac{m_1 + k_2}{m_2 - m_1} e^{m_1 t} - \frac{m_2 + k_2}{m_2 - m_1} e^{m_2 t} \qquad (8)$$

where m_1 and m_2 are the roots of the equation

$$m^2 + (k_1 + k_2 + k_3)m + k_2k_3 = 0$$

$$x = 1 - \frac{m_2 + k_1}{m_2 - m_1} e^{m_1 t} + \frac{m_1 + k_1}{m_2 - m_1} e^{m_2 t} \qquad (9)$$

where m_1 and m_2 are the roots of the equation

$$m^2 + (k_1 + k_2 + k_4)m + k_1k_4 = 0$$

A test was made of the values of k_1 and k_2 in Table III by first choosing k_3 and k_4 so as to give the right magnitude for the drift at the larger values of t, and then varying k_1 and k_2 from the values shown in Table III, so as to obtain the best agreement between x calculated and x observed. When several of the runs were thus treated, k_3 and k_4 amounted to several per cent. of $(k_1 + k_2)$. Assuming that the drift was due entirely to aldol, k_1 was left unaffected, and k_2 tended to increase by as much as 3%. Assuming that the drift was due entirely to crotonaldehyde, k_1 tended to decrease by as much as 3%, and k_2 to increase by as much as 4%; ϵ was therefore reduced by as much as 0.015. These possible corrections were in one direction and did not affect any trends mentioned. In the development of this phase of the work the authors were guided by the advice of Professor R. G. Dickinson, whose aid is gratefully acknowledged.

Hydration of Crotyl Alcohol and Crotonic Acid.—Crotyl alcohol[10] and *trans*-crotonic acid were dissolved in nitric acid solution. The former in 0.6 *N* acid decreased in unsaturation less than 0.2% per day, and the latter in 1.5 *N* acid less than 0.3% per day. It is therefore evident that of the series of compounds having similar structure, *viz.*, 2-butene, crotyl alcohol, crotonaldehyde, and crotonic acid, crotonaldehyde is the only substance which hydrates in dilute aqueous solutions of acids at ordinary temperatures.

Summary

Crotonaldehyde is reversibly hydrated to aldol in dilute aqueous solutions of acids. Hydration is first order with respect to acid and crotonaldehyde. Dehydration of aldol is first order with respect to acid and aldol. Energies of activation for hydration and dehydration are 18.23 and 24.48 kcal., respectively. Equilibrium is reached when 47% of the crotonaldehyde has been converted to aldol at 25° and 39% at 35°.

Crotyl alcohol and *trans*-crotonic acid do not hydrate at an appreciable rate at 25° in dilute aqueous nitric acid.

PASADENA, CALIF. RECEIVED MAY 11, 1937

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[9] Eberz and Lucas, THIS JOURNAL, **56**, 1230 (1934).

[10] Kindly supplied by Dr. W. G. Young of the University of California at Los Angeles.

II

THE COORDINATION OF SILVER ION WITH UNSATURATED MOLECULES

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 633]

The Coördination of Silver Ion with Unsaturated Compounds

BY SAUL WINSTEIN AND HOWARD J. LUCAS

One of the interesting properties of substances having an ethylenic linkage is the ability to form compounds of comparatively low stability. Such compounds are best termed "addition" or "coordination" compounds. They are distinctly different in type from the stable addition compounds produced by the action of the usual reagents, such as the halogens. Some compounds previously described probably belong to the coordination type, for example, the complex salts of hydrocarbons with aluminum and ferric chlorides,[1] the loose addition compounds of olefins with (a) hydrogen bromide, of the type $C_2H_4 \cdot HBr$,[2] (b) zinc chloride, of the type $C_5H_{10} \cdot ZnCl_2$[3] and the addition compounds of aromatic hydrocarbons with nitro compounds.[4] In the complex iron compound, $FeC_4H_6(CO)_3$, in which two of the five molecules of carbon monoxide of iron carbonyl are replaced by one molecule of butadiene, the unsaturated hydrocarbon satisfies one or two coordination positions of the iron atom.[5]

Cuprous, silver, and mercury salts are used for absorbing olefins.[6,7] Ethylene appears to form a loose chemical compound with cuprous chloride.[8] Addition compounds of olefins with platinous halides of the types $PtCl_2 \cdot C_2H_4$ and $KPtCl_3 \cdot C_2H_4$, known for over a century,[9] have been the subject of renewed interest lately.[10]

An understanding of the nature of the coordination bond in these olefin–metal complexes requires additional data. In this investigation, a

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[1] (a) Henderson and Gangloff, THIS JOURNAL, **39**, 1420 (1917); (b) Hunter and Yohe, *ibid.*, **55**, 1248 (1933); (c) Egloff, Wilson, Hulla and Van Arsdell, *Chem. Rev.*, **20**, 345 (1937).

[2] Maass and Wright, THIS JOURNAL, **46**, 2664 (1924).

[3] Kondakow, *Chem. Listy*, **24**, 1 (1930).

[4] Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, p. 264.

[5] Reihlen, *Ann.*, **482**, 161 (1930).

[6] Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, N. Y., 1934, pp. 142, 582.

[7] Eberz, Welge, Yost and Lucas, THIS JOURNAL, **59**, 45 (1937).

[8] Manchot and Brandt, *Ann.*, **370**, 286 (1911).

[9] Zeise, *Pogg. Ann.*, **21**, 497 (1831); Birnbaum, *Ann.*, **145**, 67 (1868).

[10] (a) Pfeiffer and Hoyer, *Z. anorg. allgem. Chem.*, **211**, 241 (1933); (b) Anderson, *J. Chem. Soc.*, 971 (1934); (c) Anderson, *ibid.*, 1042 (1936); (d) Kharasch and Ashford, THIS JOURNAL, **58**, 1733 (1936).

continuation of the work previously described,[7] the complexes between silver ion and a number of unsaturated compounds have been studied by the distribution method. In all cases it has been found that the reaction to form the complex is *rapid* and *reversible*. The conclusion can be drawn that complex formation with aqueous silver ion is a general property of compounds having an ethylenic linkage. Solid addition compounds of dicyclopentadiene with silver nitrate and perchlorate, and of biallyl with silver perchlorate, have been prepared. These solids are not very stable.

The Distribution Method.—The procedure consists in distributing the organic compound between carbon tetrachloride and 1 N potassium nitrate, and then combining the resulting distribution ratio with other data obtained by distributing the same unsaturated compound between carbon tetrachloride and 1 N silver nitrate, or a solution of both potassium nitrate and silver nitrate whose total ionic strength is 1 N. The data needed are the concentrations of the unsaturated compound in the two phases and the concentration of the silver salt in the aqueous phase. In some cases, first and second equilibrium constants can be secured. In the calculations, the following notations are used:

B = unsaturated substance
(Bt) = total concentration of unsaturated substance in aqueous phase in moles per liter
(B) = uncomplexed unsaturated material in aqueous phase in moles per liter
(BAg) = concentration of species $(B \cdot Ag)^+$ in aqueous phase, in moles per liter
(BAg_2) = concentration of species $(Ag \cdot B \cdot Ag)^{++}$ in aqueous phase in moles per liter
(B_2Ag) = concentration of species $(B \cdot Ag \cdot B)^+$ in aqueous phase in moles per liter
(Ag^+) = concentration of free silver ion in aqueous phase in moles per liter
(Agt) = total silver concentration in aqueous phase in moles per liter
$(B)_c$ = concentration of unsaturated material in carbon tetrachloride in moles per liter
μ = ionic strength = normality
K_D = $(B)_c/(B)$ = distribution ratio of the unsaturated material between carbon tetrachloride and 1 N potassium nitrate
$K = \dfrac{K_D[(Bt) - (B)]}{(B)_c[(Agt) - (Bt) + (B)]} = \dfrac{K_D[(Bt) - (B)_c/K_D]}{(B)_c[(Agt) - (Bt) + (B)_c/K_D]}$ = evaluated constant
K_1 = $(BAg)/(B)(Ag^+)$ = first argentation constant of an unsaturated material = first coördination constant of silver ion for the unsaturated substance
$K_0 = K_1/K_D$
$K_2 = \dfrac{(BAg_2)}{(BAg)(Ag^+)}$ = second argentation constant of an unsaturated substance.
$K_2' = \dfrac{(B_2Ag)}{(BAg)(B)}$ = second coördination constant of silver ion for the substance in question.

The Distribution Ratios.—The values obtained at 25° for the distribution of a number of unsaturated compounds between carbon tetrachloride and 1 N potassium nitrate are shown in Table I with the per cent. mean deviation of several determinations.

TABLE I

DISTRIBUTION RATIOS OF UNSATURATED SUBSTANCES BETWEEN CARBON TETRACHLORIDE AND 1 N POTASSIUM NITRATE AT 25°

Substance	$(B)_c$	K_D	Accuracy, %
Isobutene[7]	0.7–1.1	830	1
Trimethylethylene	1.9	2165	2
	1.5	2560[a]	3.5
2-Pentene	1.3	3860	6
Cyclohexene	1.3	4305	1
	1.1	4240[a]	7
Dimethylbutadiene	1.2	3290	1
Biallyl	0.5	4680	1
1-Hexene	1.1	9050	5
Allyl alcohol	0.005–0.02	0.0806	0.3
Crotyl alcohol	.008– .03	.365	1.5

[a] These values are for 0° instead of 25°.

With phenol and crotonic acid the situation is complicated by association in the carbon tetrachloride phase, presumably due to hydrogen bond formation. In the case of phenol (Table X) plotting $1/K_D$ against $(B)_c$ gives a curve which is almost a straight line; from this, $1/K_D$ can be obtained quite accurately for each $(B)_c$ wanted. In this way, values were estimated for $1/K_D$ for use in calculating K in the distributions of phenol between carbon tetrachloride and aqueous silver nitrate.

Crotonic acid apparently exists in the carbon tetrachloride mostly as dimer with some monomer. On this basis, (B), in the distributions when silver nitrate was present, was calculated from $(B)_c$ and the data from distributions without silver.

The Equilibrium Constants.—When only one reaction occurs in the aqueous phase between silver ion and the unsaturated substance, such as the one shown in equation (1)

$$B + Ag^+ \overset{K_1}{\rightleftarrows} BAg^+ \qquad (1)$$

the evaluated constant K is identical with the equilibrium constant, K_1. In case a subsequent reaction takes place in the aqueous phase, involving two silver ions and one unsaturated molecule, for example an alkadiene (equation 2), or involving two unsaturated molecules, for example phenol and one silver ion (equation 3)

$$\mathrm{BAg^+ + Ag^+ \overset{K_2}{\rightleftarrows} AgBAg^{++}} \qquad (2)$$

$$\mathrm{BAg^+ + B \overset{K_2'}{\rightleftarrows} BAgB^+} \qquad (3)$$

it can be shown that K is related to the first and second equilibrium constants (equations 4 and 5).

$$K = [K_1 + K_1K_2(\mathrm{Ag^+})]/[1 + K_1K_2(\mathrm{B})(\mathrm{Ag^+})] \qquad (4)$$

$$K = [K_1 + 2K_1K_2'(\mathrm{B})]/[1 - K_1K_2'(\mathrm{B})^2] \qquad (5)$$

In the case of hydrocarbons, there are several reasons for considering another constant, *viz.*, $K_0 = K_1/K_D$. Here K_0 is the equilibrium constant for the reaction between B, dissolved in carbon tetrachloride, and aqueous silver ion to give aqueous complex ion, $\mathrm{B{\cdot}Ag^+}$. Since (B) is quite small compared to (Bt), the value of K_0 is essentially independent of K_D, a constant which may be somewhat in error in some cases because of the difficulty of measurement of very high distribution ratios. In comparing stabilities of different olefin complexes, K_0 is useful because we have called unit activity of B the activity of B in a 1 M solution of B in carbon tetrachloride. Since Raoult's law is expected to hold fairly well and the solutions were not tremendously concentrated, this amounts to choosing a standard state for all the olefins with about the same activity relative to the liquid state.

The influence of partial miscibility of the solvents upon the value of the constant K_1 must be considered. K_1 is undoubtedly lower than the value for carbon tetrachloride-free water due to the increase of solubility of an olefin in water on saturating the water with carbon tetrachloride. On the other hand, K_0 is subject to no such error. If the proper data become available, K_0 could be used for calculating K_1 in carbon tetrachloride-free water.

The Argentation Constant of Monoölefins.—The data obtained with two monoölefins, *viz.*, trimethylethylene and cyclohexene, are typical. The values at 25 and 0°, respectively, are given in Tables II, III, IV and V. Inspection of the data shows that K and K_0 are fairly insensitive to variations in the concentration of both silver ion and hydrocarbon. This proves that in a molecule of the complex there is one silver ion and one molecule of unsaturated compound. On closer examination of the results, it is evident that whereas K and K_0 are independent of $(\mathrm{B})_c$ they decrease when (Agt) is made smaller. This trend was noted previously in the case of isobutene;[7] it reaches the value of 10% with the olefins of larger molecular weight. There are two possible expla-

TABLE II

DISTRIBUTION AT 25° OF TRIMETHYLETHYLENE BETWEEN CARBON TETRACHLORIDE AND $\mathrm{AgNO_3 + KNO_3{\cdot}Aq}$, $\mu = 1\ N$

$\mathrm{AgNO_3}$ (Agt)	Molal concn. of $\mathrm{C_5H_{10}}$ in $\mathrm{CCl_4}$ $(\mathrm{B})_c$	$\mathrm{H_2O}$ (Bt)	K	K_0
1.000	1.896	0.01264	13.6	0.00628
1.000	0.732	.00482	13.3	.00615
1.000	0.366	.00244	13.4	.00620
0.715	1.908	.00918	13.3	.00615
.500	1.908	.00647	12.8	.00592
.285	1.925	.00422	13.2	.00610
		Mean	13.3 ± 0.2	0.00613 ± 0.00008

TABLE III

DISTRIBUTION AT 0° OF TRIMETHYLETHYLENE BETWEEN CARBON TETRACHLORIDE AND $\mathrm{AgNO_3 + KNO_3{\cdot}Aq}$, $\mu = 1\ N$

$\mathrm{AgNO_3}$ (Agt)	Molal concn. of $\mathrm{C_5H_{10}}$ in $\mathrm{CCl_4}$ $(\mathrm{B})_c$	$\mathrm{H_2O}$ (Bt)	K	K_0
1.000	1.378	0.02219	40.3	0.0157
1.000	0.715	.01143	40.5	.0158
1.000	.358	.00584	42.4	.0165
0.500	1.434	.01113	38.7	.0151
.250	1.461	.00566	36.3	.0142
		Mean	39.6 ± 1.7	0.0155 ± 0.0006

TABLE IV

DISTRIBUTION AT 25° OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND $\mathrm{AgNO_3 + KNO_3{\cdot}Aq}$, $\mu = 1\ N$

$\mathrm{AgNO_3}$ (Agt)	Molal concn. of $\mathrm{C_6H_{10}}$ in $\mathrm{CCl_4}$ $(\mathrm{B})_c$	$\mathrm{H_2O}$ (Bt)	K	K_0
1.000	1.316	0.02510	83.1	0.0193
1.000	0.554	.01040	81.0	.0188
1.000	.276	.00530	82.2	.0191
0.715	1.330	.01742	79.3	.0184
.500	1.330	.01193	77.1	.0179
.250	1.337	.00584	73.2	.0170
		Mean	79.3 ± 2.8	0.0184 ± 0.0006

TABLE V

DISTRIBUTION AT 0° OF CYCLOHEXENE BETWEEN CARBON TETRACHLORIDE AND $\mathrm{AgNO_3 + KNO_3{\cdot}Aq}$, $\mu = 1\ N$

$\mathrm{AgNO_3}$ (Agt)	Molal concn. of $\mathrm{C_6H_{10}}$ in $\mathrm{CCl_4}$ $(\mathrm{B})_c$	$\mathrm{H_2O}$ (Bt)	K	K_0
1.000	0.943	0.0433	203	0.0478
1.000	.580	.0231	192	.0453
1.000	.260	.0119	196	.0462
0.500	1.046	.0226	188	.0443
.250	1.103	.01125	176	.0415
		Mean	191 ± 7	0.0450 ± 0.0017

nations of this phenomenon: (a) some of the one-to-one complex reacts with more silver ion (equation 2) or (b) the ratio of the activity coefficients of Ag^+, and $B{\cdot}Ag^+$ exhibits a trend as silver nitrate is replaced by potassium nitrate. The latter explanation seems more reasonable.

The argentation constants of the hydrocarbons investigated are shown in Table XII. In the case of 2-pentene, which probably was largely the *trans* isomer,[11] a good constant was obtained. Even if the sample were a mixture of approximately equal parts of the *cis* and *trans* forms, a satisfactory constant would be expected, because (Bt) is quite small compared to $(B)_c$, making the composition of olefin in the carbon tetrachloride essentially constant and equal to the original composition.

The Argentation Constants of Dienes.—The data obtained with two dienes, *viz.*, 2,3-dimethylbutadiene-1,3 and biallyl are shown in Tables VI and VII. Here the large trends in K must arise from the ability of the hydrocarbon molecule to coördinate with two silver ions (equation 2). The values for K_1 and K_2 were obtained by successive approximations, using equations 4 and 6.

$$(Ag^+) = (Agt) - K_1(B)(Ag^+) - 2K_1K_2(B)(Ag^+)^2 \quad (6)$$

Figure 1 shows a plot of $[1 + K_1K_2(B)(Ag^+)]K$ against (Ag^+). Table VI also contains the individual values of K_2 calculated using the intercept value of 22.5 for K_1.

TABLE VI

DISTRIBUTION AT 25° OF DIMETHYLBUTADIENE BETWEEN CARBON TETRACHLORIDE AND $AgNO_3 + KNO_3{\cdot}Aq$, $\mu = 1\ N$

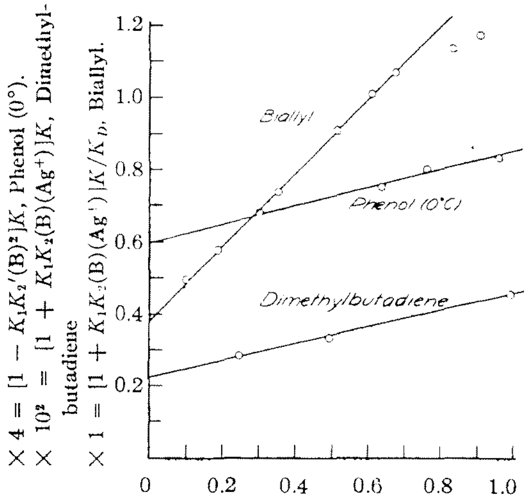
$AgNO_3$ (Agt)	Molal concn. of C_6H_{10} in CCl_4 $(B)_c$	H_2O (Bt)	K	K_1	K_2
1.000	1.121	0.01575	45.9	22.5	1.08
1.000	0.581	.00775	43.3		0.96
1.000	.290	.00415	46.2		1.07
0.500	1.169	.00617	33.2		0.98
.250	1.186	.00286	28.1		1.03
			Mean	22.5	1.02±0.04

TABLE VII

DISTRIBUTION AT 25° OF BIALLYL BETWEEN CARBON TETRACHLORIDE AND $AgNO_3 + KNO_3{\cdot}Aq$, $\mu = 1\ N$

$AgNO_3$ (Agt)	Molal concn. of C_6H_{10} in CCl_4 $(B)_c$	H_2O (Bt)	(Bt) calcd.	$K \times 10^{-3}$
1.000	0.281	0.2024	0.199	4.23
1.000	.0987	.0945	.0982	4.92
1.000	.0468	.0500	.0536	5.27
0.750	.330	.1530	.1515	3.64
.500	.383	.1001	.0998	3.06
.250	.436	.0472	.0472	2.50
.125	.461	.0224	.0223	2.22

$K_1 = 1.85 \times 10^3$ $K_2 = 2.43$



$\times 1 = (Ag^+)$, Biallyl and dimethylbutadiene.
$\times 10^{-1} = (B)$, Phenol (0°).

Fig. 1.

The data for biallyl were treated similarly. Figure 1 contains a plot of $[1 + K_1K_2(B)(Ag^+)]K/K_D$ against (Ag^+) and Table VII contains a comparison between the observed values of (Bt) and those calculated from equation 7.

$$(Bt) = (B)[1 + K_1(Ag^+) + K_1K_2(Ag^+)^2] \quad (7)$$

Oxygenated Compounds and the Second Coördination Constant of Silver Ion.—Several oxygenated unsaturated compounds were studied, and of these the data for crotyl alcohol and phenol are given.

The data for crotyl alcohol and phenol, at 25°, are shown in Tables VIII and IX, respectively. The fair constancy in the values of K indicates that only one complex ion is formed in appreciable amounts at 25° in each case. In the case of phenol there may be a tendency for a trend in K with (B) but it is small and irregular due to experimental variation. At 0°, however (Table XI), this trend is quite pronounced, showing that silver ion definitely coördinates with two molecules of phenol according to equation 3.

The relation between K, K_1, K_2' and (B) is given by equation 5. Neglecting $K_1K_2'(B)^2$ compared to unity, approximate values of K_1 and K_2' may be obtained. The plot of $[1 - K_1K_2'(B)^2]K$ against (B), Fig. 1, gives K_1 and $2K_1K_2'$ as the intercept and slope, respectively. Using

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[11] Lucas and Prater, THIS JOURNAL, 59, 1682 (1937).

TABLE VIII

DISTRIBUTION AT 25° OF CROTYL ALCOHOL BETWEEN CARBON TETRACHLORIDE AND $AgNO_3$ + KNO_3·Aq, μ = 1 N

$AgNO_3$ (Agt)	Molal concn. of C_4H_7OH in CCl$_4$ $(B)_c$	H_2O (Bt)	K
1.000	0.00813	0.1209	4.92
0.715	.01324	.1534	5.39
.500	.01189	.1047	5.17
.285	.02706	.1533	5.18
		Mean	5.17±0.12

TABLE IX

DISTRIBUTION AT 25° OF PHENOL BETWEEN CARBON TETRACHLORIDE AND $AgNO_3$ + KNO_3·Aq, μ = 1 N

$AgNO_3$ (Agt)	Molal concn. of C_6H_5OH in CCl$_4$ $(B)_c$	H_2O (Bt)	K
1.000	0.0349	0.1731	2.34
1.000	.0190	.0961	2.15
1.000	.0162	.0829	2.13
1.000	.0069	.0366	2.10
0.715	.0326	.1268	2.16
.500	.0286	.0929	2.14
.285	.0442	.1102	2.33
		Mean	2.19±0.08

the intercept value of 2.42 for K_1, calculated values of K_2' are obtained, as shown in Table XI.

TABLE X

DISTRIBUTION OF PHENOL BETWEEN 1 N POTASSIUM NITRATE AND CARBON TETRACHLORIDE

$(B)_c$	(B)	$1/K_D$
	25°	
0.04700	0.07460	1.585
.01676	.02853	1.703
.00688	.01205	1.753
	0°	
0.0315	0.0846	2.68
.01065	.03153	2.96
.00447	.01343	3.01

TABLE XI

DISTRIBUTION AT 0° OF PHENOL BETWEEN CARBON TETRACHLORIDE AND $AgNO_3$ + KNO_3·Aq, μ = 1 N

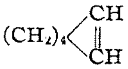
$AgNO_3$ (Agt)	Molal concn. of C_6H_5OH in CCl$_4$ $(B)_c$	H_2O (Bt)	K	K_1	K_2'
1.000	0.0102	0.1059	2.72	2.42	1.98
0.750	.0227	.1867	3.07		1.91
.500	.0279	.1762	3.28		2.08
.250	.0368	.1585	3.47		1.94
			Mean	2.42	1.98±0.05

In the case of allyl alcohol at 25°, there was a trend in K with (B), similar to the one of phenol at 0°. The values of the constants, shown in Table XIII, are not as satisfactory as the phenol constants.

When K_1 of oxygenated compounds is quite small, as in the case of crotonaldehyde, crotonic acid and acetone, it becomes difficult to obtain K_1 with accuracy, or even to say with certainty that complex formation takes place. This is because (B) is almost equal to (Bt), and (B) depends upon K_D, which must be assumed to remain constant at constant ionic strength, *i. e.*, that potassium and silver ions are equivalent in their effect upon the activity of the unsaturated substance. The values of K_1 for several oxygenated compounds investigated, are summarized in Table XIII.

TABLE XII

SUMMARY OF CONSTANTS FOR OLEFIN–SILVER ION COMPLEXES AT 25°

Substance	K_1	K_2	K_0
$H_2C{=}CH(CH_2)_2CH{=}CH_2$	1850	2.43	0.395
n-$BuCH{=}CH_2$	860		.095
$Me_2C{=}CH_2$	61.7		.0743
$EtCH{=}CHMe$	62.7		.0162
	79.3		.0184
	191[a]		.0450[a]
$Me_2C{=}CHMe$	13.3		.00613
	39.6[a]		.0155[a]
$H_2C{=}CMeCMe{=}CH_2$	22.5	1.02	.00684
$C_6H_5CH{=}CHMe$			.0018

[a] These values are at 0° and not 25°.

TABLE XIII

SUMMARY OF CONSTANTS FOR SILVER COMPLEXES OF OXYGEN-CONTAINING COMPOUNDS AT 25°

Substance	K_1	K_2'
$H_2C{=}CHCH_2OH$	12	3
$MeCH{=}CHCH_2OH$	5.17	
$MeCH{=}CHCHO$	0.19	
$MeCH{=}CHCOOH$	.09	
Me_2CO	.14	
C_6H_5OH	2.19	
	2.42[a]	1.98[a]

[a] These values are at 0° and not 25°.

Thermochemical Data.—In the case of trimethylethylene and cyclohexene the distributions were done at 25 and at 0°. From the respective K_0 values (Table XIV), the calculated $-\Delta H$ for the change shown in equation 8, is approximately 6.0 kcal.

$$B_c + Ag^+_{Aq} \overset{K_0}{\rightleftarrows} BAg^+_{Aq} \qquad (8)$$

Since K_D changes but slightly between 25 and 0° (Table I), 6 kcal. is approximately the heat effect attending the formation of one mole of complex in aqueous solution, that is, for the reaction of which K_1 is the equilibrium constant. This value is comparable to -6.7 kcal., one-half the ΔH for the coördination of two ammonia molecules with one silver ion in aqueous solution.[12]

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[12] Smith, Brown and Pitzer, THIS JOURNAL, **59**, 1213 (1937).

TABLE XIV

TEMPERATURE COEFFICIENTS AND HEAT EFFECTS FOR TRIMETHYLETHYLENE AND CYCLOHEXENE

Substance	K_0/K_{25}	$-\Delta H$, kcal.
C_5H_{10}	2.53	6.01
C_6H_{10}	2.45	5.80

The chemical change which takes place when the complex is formed is probably the replacement of a coördinated water molecule by the ethylene molecule (Equation 9), for the silver ion in water solution apparently has two water molecules coördinated with it.[13] If the strength of the coördination bond holding a water molecule is much greater than that of the one holding the olefinic compound, there will be little or no tendency for the latter to form a complex with the silver ion.

$$B + (H_2O)_2 \cdot Ag^+ \overset{K_1}{\rightleftarrows} B(H_2O)Ag^+ + H_2O \quad (9)$$

The inability of many metallic ions which readily coördinate with ammonia, etc., to form complexes with ethylenic compounds in aqueous solution may be due to this difference rather than to a pronounced weakness of the coördinated metal–olefin bond. Of the ten metallic ions studied in this work, silver was the only one which entered into complex formation. Five of the nine non-complex-forming ions have been noted previously,[14] not to influence the rate of hydration of isobutene, whereas the rate was lowered in the presence of silver, which forms a complex. The rate dropped also when a mercuric salt was present, probably because mercuric ion also forms complexes with isobutene.[15]

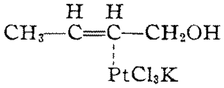
The energy of the bond between silver and the unsaturated compound is probably somewhat greater than 6 kcal., for to the $-\Delta H$ of the reaction shown in equation 9, must be added the $-\Delta H$ of the reaction shown in equation 10.

$$H_2O + H_2O \cdot Ag^+ \rightleftarrows (H_2O)_2Ag^+ \quad (10)$$

Discussion

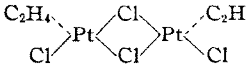
Nature of the Silver–Olefin Coördination Bond.—This bond is probably similar in character to the coördination bond of other metals with olefins. The question as to the nature of the binding has been a difficult one, due to the absence of a "lone pair" of electrons, through which bond formation might be thought to take place.

Pfeiffer and Hoyer,[10a] in the Zeise salt complex of crotyl alcohol, regard the platinum as coördinated with the double bond, according to I below. Anderson[10b] showed that ethylene platinous chloride has double the simple molecular weight, and formulated the compound as a quadricovalent platinum complex in which each chlorine atom forms two coördinate links and the ethylene molecule satisfies one coördination position on the platinum atom (II). Kharasch and Ashford[10d] have objected to such a formula on the ground that chlorine cannot form two such links, and have proposed the ring structure, III. In his second paper Anderson[10c] suggested that the only way a lone pair of electrons can be generated for coördination purposes is to activate the double bond to give the structure IV. Although he did not actually write a structure for the complex, the one shown as V was indicated.

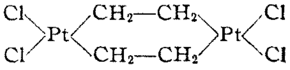


$$CH_3—\overset{H}{C}=\underset{\vdots \atop PtCl_3K}{\overset{H}{C}}—CH_2OH$$

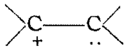
I



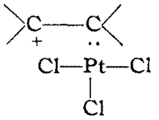
II



III



IV



V

Anderson believes coördination through such an intermediate as IV is improbable because a high energy of activation would be required, and therefore a slow reaction would be expected. Also, such a mechanism would give ample opportunity for polymerization and rearrangement. On the other hand, in the formation of V it is not necessary that IV be an intermediate. However, a structure for the complex with one carbon atom having only a sextet of electrons is unlikely, for such compounds are easily formulated to lead to polymerization and rearrangement.[1b,16] There was an absence of polymerization in the platinum work, and in the present silver work. Also, *cis*- and *trans*-2-butenes were not rearranged in the least by the action of aqueous silver nitrate, as described later.

In order to account for rapid, reversible reactions and absence of rearrangement, one must look for a structure which is neither of the quadrivalent platinum type (*i. e.*, like III), nor of the type in which the double bond has been opened (IV or V). Still, one would like to have the co-

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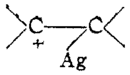
(13) Schmidt and Keller, *Z. physik. Chem.*, **A141**, 331 (1929).

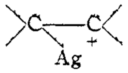
(14) Lucas and Eberz, THIS JOURNAL, **56**, 460 (1934).

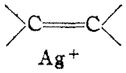
(15) A study of mercuric complexes with unsaturated compounds by the distribution method is contemplated in this Laboratory.

(16) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

ordination link retain, as much as possible, the character of usual coördination links (electron-pair bonds). A satisfactory structure is obtained by considering the possibility of resonance[17] among the three forms, VI, VII, and VIII:


VI


VII


VIII

The formation of a hybrid structure made up of contributions from these three forms need not go through an intermediate containing an activated double bond. Resonance among the three forms prevents the complex from behaving as a molecule having one carbon with just a sextet of electrons. Thus the characteristic properties of the silver and platinum complexes seem reasonable, *i. e.*, rapid reversible reactions but no polymerization and rearrangement.

The objection might be raised to the formation of what amounts to a three-membered ring on the basis of strain involved, but this objection is soon seen not to be very serious. Only the strain at one carbon atom need be considered. Since the C–C–Ag bond angle will be considerably larger than the 60° angle of cyclopropane, the strain will be very much less than one-third of the total strain in the cyclopropane ring, due to the fact that the strain decreases quite rapidly as the bond angle increases. The resonance energy, about 10 kcal., is enough greater than the strain energy, probably 3 to 4 kcal., to lead to an expectation of moderate stability.

We believe that the formula proposed by Anderson for ethylene platinous chloride, II, is preferable to the one by Kharasch and Ashford, III. From a purely chemical point of view, one would not expect ethylene platinous chloride, potassium ethylenetrichloroplatinite, and other similar compounds to undergo so many reactions typical of compounds having a coördination link, if the carbon-to-metal bond were a metallo-organic bond of the type characteristic of III. There is really no objection to two coördinate links for chlorine, since stable compounds are known in which halogen atoms have two such bonds.[18,19]

Extending the concept of resonance to potassium ethylenetrichloroplatinite one should write, in addition to V, the two other electronic forms which are analogous to VII and VIII. In the case of ethylene platinous chloride, the possibility of resonance among nine electronic forms of structure II is a factor which enhances the stability of this compound.

Since aromatic compounds can form complexes also, it is evident that an aromatic ring can replace the ethylenic linkage in complex formation. For the complex between benzene and an ion, such as silver ion, the ion is on the sixfold symmetry axis of the benzene ring. This conforms with the dome-like structure of the benzene molecule proposed by Mack.[20] The silver may be bonded to any one of the six carbon atoms, giving rise to eighteen bonded and two unbonded forms.

Other Olefinic Coördination Bonds.—The above idea of the coördination link between unsaturated compounds and other atoms is capable of general application. It seems probable that resonance involving more than one electronic form is a general property of this interesting group of complexes, and would apply to those containing anhydrous hydrogen halides, anhydrous aluminum and ferric chlorides, iron carbonyl residues, cuprous salts and other atoms.

This picture of the coördination bond of unsaturated compounds can be applied to the formulation of complexes between aromatic hydrocarbons and nitro compounds. Amplifying the structure suggested by Bennett and Willis[21] there are eight unbonded and thirty-six bonded forms in the case of a complex between an aromatic compound having one benzene ring and a mono-nitro benzene compound. Such multiplicity is probably the factor which is responsible for the stability of these nitro complexes. It is obvious that the presence of more nitro groups or of more benzene rings in the complex, will greatly increase the number of resonating forms.

The existence of intermediate complexes of the general type, $C_2H_4Br^+$, has been postulated in addition reactions of ethylenic compounds with the halogens.[22] In many addition reactions of hydrogen halides to olefinic bonds, Kharasch[23] and co-workers have found that oxygen (and peroxides) have both an activating and directing

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[17] This concept developed during a conference with Professor Linus Pauling. We are also indebted to him for estimates of resonance and strain energies.

[18] Palmer and Elliott, paper to be published in THIS JOURNAL.

[19] Gibson and Simonsen, *J. Chem. Soc.*, 2531 (1930); see also Mann and Purdie, *ibid.*, 873 (1936).

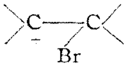
[20] Mack, *J. Phys. Chem.*, **41**, 222 (1937).

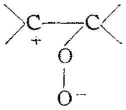
[21] Bennett and Willis, *J. Chem. Soc.*, 258 (1929).

[22] Terry and Eichelberger, THIS JOURNAL, **47**, 1415 (1925); Ingold, *Chem. Rev.*, **15**, 225 (1934); Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936); Tarbell and Bartlett, *ibid.*, **59**, 407 (1937).

[23] Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937), and numerous previous papers.

influence. The positive bromide complex is probably strictly analogous to the silver ion complex (one form only shown, as IX), and the oxygen intermediate can be represented in the same way (X). A modified form of the latter is XI. We believe that the directive influence of oxygen in the abnormal additions of hydrogen bromide to the double bond, is due to the fact that in the complex the contributions of the bonded forms X and XI, in which oxygen occupies the position which the proton would normally take, (XII), are more important. The proton can combine with the oxygen complex (at the negative carbon of XI) and an exchange can take place between halide ion and oxygen, thus giving rise to a product different from the result of normal addition.


IX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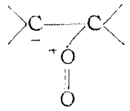
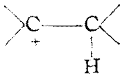

XI


XII

The complex resulting from the conjugation of the proton with the double bond may be formulated as XII. This is probably the critical complex involved in the hydration of isobutene and other unsaturated compounds. Presumably it is the first step in the addition of hydrogen halides (normal reaction, in the absence of oxygen), hydrogen sulfate, etc., to the double bond, and in the polymerizing action of the latter. It is probably an intermediate also in the dehydration of alcohols,[16,24] the dehydrohalogenation of alkyl halides, etc. The low stability of this type of complex is indicated by the fact that evidence for the existence of the compound $C_2H_4 \cdot HBr$ is obtained only at low temperatures[2] (*ca.* $-160°$).

In general, the complexes of different types, with the exception of the proton type, appear to be moderately stable. The greatest differences lie in reactivity. From theoretical considerations, generalizations in regard to reactivity may be made, as follows: (a) the smaller the coördinated atom the greater the reactivity; (b) the more electronegative the coördinated atom the greater the reactivity. The covalent radii of the atoms decrease in the order Ag, Pt, Al, Br, O, H;[25] the electronegativities increase in the order, Al, H, Br, N, O.[26] The relatively low reactivities of the silver and platinum complexes (absence of polymerization and isomerization) are probably due to the comparatively large size of these metal atoms. Just how the two factors, size and electronegativity, influence the contribution to the total structure made by the three different forms analogous to VI, VII and VIII is a matter of speculation. It seems likely that high reactivity may be associated with a system in which the main contribution to the structure is made by only one form, or perhaps two forms. Thus, in the proton complex, it is hardly reasonable to expect contributions from both the forms analogous to VI and VII, respectively, because of the large strain.

Influence of Structure upon the Stability of the Silver Complexes.—It is apparent from Table XII that K_0 is less, the more deeply the double bond is buried in the carbon chain. For the dienes, one should consider one-half of K_0. Thus the value is highest for biallyl and 1-hexene, with terminal double bonds, next highest for isobutene, with a terminal double bond and a tertiary unsaturated carbon atom, and much lower for 2-pentene and cyclohexene, with non-terminal double bonds. The value is lowest for trimethylethylene, with a non-terminal double bond and a tertiary unsaturated carbon atom. In agreement with Anderson[10c] it is believed that the influence of structure upon stability is probably steric in nature.

Conjugation markedly affects the value of K_0. Solely on the basis of the argument above, dimethylbutadiene would be expected to have a value about twice that of isobutene, *i. e.*, about 0.15, instead of the actual value of 0.0068, and propenylbenzene would be expected to have a value similar to that of cyclohexene, *i. e.*, about 0.018 instead of 0.0018, if the assumption is made that the side chain double bond is the reactive center. From these two examples it appears that conjugation decreases the ease of complex formation. If it is assumed that the conjugation existing in the uncomplexed dimethylbutadiene molecule disappears on adding one silver, one would predict that K_0 should be about 0.001 of the value estimated from the K_0 of isobutene, due to the fact that $-\Delta H$ of conjugation[27] and presumably $-\Delta F$ is approximately 4 kcal. The experimental ratio of 1/22, instead of 1/1000 is understandable when one notices the extra opportunity for reso-

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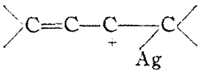
(24) Hughes, Ingold and Scott, *J. Chem. Soc.*, 1971 (1937).

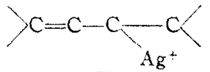
(25) Pauling and Huggins, *Z. Krist.*, **87**, 205 (1934).

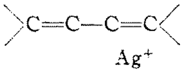
(26) Pauling, This Journal, **54**, 3570 (1932).

(27) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 152 (1936).

nance in the diene–monosilver case, compared to the monoölefin–silver complex. The forms which contribute to the structure of the diene–monosilver complex are shown as XIII to XVIII.


XIII


XIV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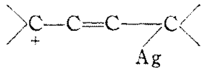
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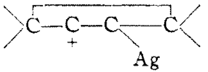
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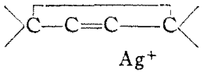
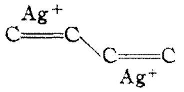
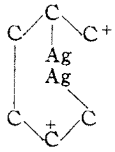

XVIII

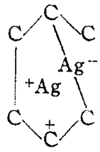
Complexes of Unsaturated Oxygen Compounds with Silver Ion.—The ability of oxygen in organic molecules to compete successfully with the oxygen of water for the coördination position on the silver atom is, at the best, quite weak, for acetone, which might be expected to do this, forms very little complex (Table XIII). Moreover, saturated analogs of allyl alcohol, crotyl alcohol, crotonaldehyde, etc., do not form complexes with platinum compounds whereas the unsaturated compounds do.[10a] It seems reasonable to ascribe the complex forming ability of the unsaturated oxygenated compounds, therefore, to the ethylenic bond. In the case of phenol, the ability to form complexes probably resides in the benzene ring, for silver perchlorate has a remarkably high solubility in benzene.[28] In this connection, the difference in solubility of silver nitrate and silver perchlorate in benzene is of interest, silver nitrate being insoluble. In the present work, silver perchlorate and silver nitrate gave similar results. Although unsaturation appears to be responsible for complex formation, the explanation is not unambiguous, especially in those cases where the complex is composed of one silver atom and two unsaturated, oxygenated molecules.

In the complexes with unsaturated oxygen compounds, the effects of position of the double bond, and of conjugation with a carbonyl or carboxyl group are similar to those already noted in the case of the hydrocarbons. Thus, the value of K_1 is 12 for allyl alcohol and 5 for crotyl alcohol (Table XIII); also the latter value is larger than 0.19 for crotonic aldehyde and 0.09 for crotonic acid. In the case of phenol, K_2' at 0° has about the same value as K_1, and decreases rapidly with increase in temperature. Bailey[29] has isolated the solid $(C_6H_5OH)_2 \cdot AgNO_3$ in a phase rule study of the system phenol–silver nitrate.

The Positive Charge Separation in Diene Complexes.—Applying the well-known method used in calculating the distance between the carboxyl groups of dibasic acids[30] it is possible to calculate the positive charge separation in complexes containing one molecule of diene and two silver ions. For the dimethylbutadiene complex, this value is 4.2 Å. The calculation is complicated by resonance other than that used in explaining coördination of silver with an unconjugated ethylenic linkage, but these resonance effects may tend to cancel, since such effects are probably produced with each addition of a silver ion to the diene molecule. The double bond–double bond separation in butadiene is 2.5 Å., and the silver–silver separation is 5.7 Å., using 2.12 Å. as the carbon–silver distance, in the model below (XIX). Thus 4.2 Å. is a reasonable value for it is close to the mean (4.1) of the last two figures above.


XIX


XX


XXI

For the biallyl complex, 1.4 Å. is the calculated separation of charges. This is a surprisingly low result. It may be accounted for in part by assuming that the carbon chain is bent around so that each silver ion can interact with both double bonds. When each silver has interacted with one double bond, the structure would be something like XX and when one silver interacts with two double bonds, like XXI.

Experimental

Materials.—In general, inorganic chemicals were of C. P. or reagent grade. The standard silver nitrate was made up by weight and checked against standard thiocyanate. Standard bromate–bromide solutions were made up by weight or dilution of more concentrated ones. Carbon tetrachloride was purified by saturating it with chlorine, allowing the solution to remain in the sunlight for a time, removing the chlorine, drying and distilling; b. p. 76.7° (760 mm.). A blank on the carbon tetrachloride showed that it neither used up nor liberated bromine or iodine.

Trimethylethylene was the product obtained by the careful fractionation of amylene obtained from tertiary amyl alcohol by heating with oxalic acid; b. p. 38.5–38.6°

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(28) Hill, This Journal, **44**, 1163 (1922).

(29) Bailey, *J. Chem. Soc.*, 1534 (1930).

(30) Hückel, "Theoretische Grundlagen der organischen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. II, 1935, p. 250.

(760 mm.). The purity by bromine absorption was 100.5%. The 2-butenes used in this work were mixtures of *cis*- and *trans*-2-butene contaminated with traces of 1-butene. The two samples distilled at −0.1–+0.9°, and 1.9–2.2°, respectively. 2-Pentene was obtained by dehydration of secondary amyl alcohol; b. p. 36.0–36.2° (760 mm.), after careful fractionation; purity, 100.0%. 1-Hexene was obtained by the reaction of allyl bromide and propylmagnesium bromide in dibutyl ether. The product stood with sodium until it gave no halogen test with hot alcoholic silver nitrate. The fraction, b. p. 63.2–63.7° (760 mm.) had a purity of 99.7%. Cyclohexene samples were obtained by dehydration of cyclohexanol with sulfuric acid; b. p. of two preparations, 82.7 and 82.6–82.7° (760 mm.); purity, 99.2 and 99.8%. 2,3-Dimethylbutadiene-1,3 was prepared by dehydration of pinacol with potassium acid sulfate. It distilled at 68.3–68.4° (760 mm.); purity, at least 98%. Biallyl was prepared from allyl bromide and molten sodium in butyl ether. The product was left over sodium until no halogen test was given on heating with alcoholic silver nitrate, and then carefully fractionated; b. p. 59.1–59.4° (760 mm.); purity 99.5%. Dicyclopentadiene was purified by depolymerizing technical material from the Gesellschaft für Teerverwertung, polymerizing the monomer, and distilling the dimer at reduced pressure. The product distilled at 71° (24 mm.), and melted at 32.3°. The propenylbenzene available distilled at 177–179° (760 mm.).

Allyl alcohol used was the product obtained by fractionation of Eastman material after drying over potassium carbonate; b. p. 96.4–96.7° (760 mm.); purity 99.3%. Crotyl alcohol[31] was prepared from crotonaldehyde by reduction with aluminum isopropoxide; b. p. 121.7–121.9° (760 mm.); purity 98%. Crotonaldehyde was fractionated Niacet material; b. p. 102.5–102.7° (760 mm.); purity 99.1%. Crotonic acid was twice recrystallized Eastman material; purity 99.5%. Phenol was distilled U. S. P. material, the fraction used in this work distilling at 181.2–181.3° (760 mm.); purity 99.9%. Acetone was Merck c. p. material.

Analysis.—The analysis for the ethylenic compounds was carried out, in general, by bromination with standard bromate–bromide according to the technique previously described.[7] Pure materials were analyzed by making up weighed samples to volume with carbon tetrachloride or water, and analyzing aliquot portions of the solution. For the dilute solutions, 0.05 *N* bromate–bromide and 0.02 *N* thiosulfate were used, and more concentrated reagents were employed as needed. For most substances (exceptions are discussed below), five minutes of shaking with a small excess of bromate–bromide is sufficient for analysis of both aqueous or carbon tetrachloride solutions. Longer times have no effect (within 0.2%) with the oxygen-containing substances but the hydrocarbons such as cyclohexene and trimethylethylene tended to substitute to the extent of about 0.2% per every five additional minutes, under the conditions used. The aqueous solution of crotonic acid requires ten minutes with about 50% excess bromate. In carbon tetrachloride solution it was analyzed by base titration, the bromine reaction being fairly slow. The aqueous solution of dimethylbutadiene required the addition of glacial acetic acid (approximately one-half the volume of the water) for analysis in five minutes. Without acetic acid, the titration in five minutes amounted to about 97% of the value with acetic acid, and increased with time. Bromination of the carbon tetrachloride solution of dimethylbutadiene was sluggish even with acetic acid present, but reached 98% in fifteen minutes. For the analysis of biallyl in carbon tetrachloride, acetic acid was added, and a fifteen-minute interval was necessary. A small blank correction on the acetic acid was made in the runs employing this substance.

Phenol in aqueous solution was analyzed with bromate–bromide but this method fails in the presence of carbon tetrachloride due to incomplete reaction. Acetone in aqueous solution was analyzed by a modified iodoform method: bromate–bromide solution, potassium iodide, and acid generated the excess iodine; pure acetone ran 1.5% high under these conditions in agreement with Haughton[32] and a correction was applied to the analyses.

In the analysis of solutions containing silver nitrate, there must, of course, be added enough bromide ion to precipitate all the silver and enough iodide later to take care of any metathesis of silver bromide to iodide. The presence of silver bromide and iodide produces an end-point somewhat like that in an iodimetric copper analysis.

Effect of Peroxide.—When trimethylethylene containing considerable peroxide was distributed between carbon tetrachloride and 1 *N* potassium nitrate, the water phase required about fifteen times the correct amount of bromate to leave a bromine color after addition of the water sample to the bromine. On addition of potassium iodide and back titration with thiosulfate, the iodine color recurred rapidly, the end-point drifting until most of the bromine had been regenerated as iodine. With silver nitrate present in the water, the water samples also used up considerably more bromine than the correct amount, the end-point drifting very badly. When unsaturated materials free of peroxide were used the end-points were sharp. Only freshly distilled materials (distilled from sodium whenever permissible) which gave no test for peroxide with potassium iodide, acid and starch, were used in the distribution measurements.

Distributions.—The distributions were carried out essentially as previously described,[7] except that occasional shaking by hand was substituted for mechanical stirring. In the runs without silver, flasks of about 150-ml. capacity were used, so that one run would permit one or two analyses of the aqueous phase. In the work at 0°, concentrations were still expressed in moles per liter at 25°. One hour in the thermostat at 25.0 ± 0.05° or 0.0 ± 0.05° (crushed ice-water bath) with shaking every few minutes was allowed for the establishment of equilibrium between the phases. It is difficult to determine large distribution ratios very accurately because a trace of the concentrated phase in the dilute phase gives rise to large errors and because of the small amount of reagent consumed by a convenient sample of the dilute phase. In the case of the runs with silver present, the concentration of olefin in the aqueous phase was much greater and, therefore, errors due

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(31) Kindly supplied by Dr. W. G. Young of the University of California at Los Angeles, to whom thanks are also due for other courtesies extended during this work.

(32) Haughton, *Ind. Eng. Chem., Anal. Ed.*, **9**, 167 (1937).

to improper settling out are relatively unimportant. In the case of allyl alcohol, crotyl alcohol, and phenol, the accuracy is much greater but, in the case of the latter two, there are systematic changes in K_D with concentration.

In making the distribution measurements, as for example with phenol, a standard solution of phenol in carbon tetrachloride was made up and known volumes of it or diluted material were used with known volumes of aqueous phase in the distributions. The amounts were regulated so that not too much phenol would be removed from the carbon tetrachloride. The aqueous phase was analyzed and the concentration of phenol in the carbon tetrachloride was calculated. The same procedure was used with acetone and in most of the work with olefins.

In the distributions, no detectable amount of silver entered the carbon tetrachloride phase. It was thought that possibly a reaction such as shown in equation 11

$$\mathrm{Ag^+ + B + H_2O = Ag{\cdot}B{\cdot}OH + H^+} \qquad (11)$$

might be contributing somewhat to the extraction of olefin by the aqueous phase. Experiment showed that this did not occur, for a solution of 1 *N* silver nitrate gave a *p*H of 5.3 before and after saturation with isobutene.

The respective values of $(\mathrm{B})_c$ and (Bt) for the following compounds with (a) 1 *N* potassium nitrate and (b) 1 *N* silver nitrate are: crotonaldehyde, (a) 0.0360 and 0.0160: (b) 0.0326 and 0.0172; crotonic acid (plus a small amount of nitric acid to repress ionization): 0.058 and 0.0984 (duplicate, 0.007 and 0.0300); 0.0216 and 0.0599 (0.5 *N* silver nitrate at $\mu = 1$); acetone, 0.0149 and 0.0288: 0.0140 and 0.0308; propenylbenzene, 0.77 and 0.0014 (1 *N* silver nitrate only). Extended measurements were not made with the above. No data are given for some compounds for which extended measurements were made (Table XII); in these cases the concentration ranges were similar to the ranges explored in the cases tabulated (Tables II to VIII).

Attempted Rearrangement of the 2-Butenes.—Two different liquid mixtures of the 2-butenes were each divided into two portions. One portion was shaken with aqueous 1 *N* silver nitrate for twelve hours in an ampoule. An increase of a few per cent. in the volume of the aqueous phase took place as the butene dissolved at the very beginning. After the shaking period, both the treated and untreated butenes were converted to dibromobutanes by distillation of the butenes into a bromination flask. As the butenes were distilled from the aqueous solution, considerable gas bubbled out of the solution after the butene phase was gone. Shown in Table XV are the second order reaction rate constants, k_2, for the reaction of potassium iodide with the dibromides[33] obtained from both the treated and untreated butenes; also the calculated percentages of *cis*-2-butene, neglecting the small amount of 1-butene. It is evident that, within experimental error, silver nitrate has caused no rearrangement, for no appreciable tendency toward production of an equilibrium mixture was noted.

Table XV

Effect of Silver Nitrate upon the *cis-trans* Ratio in 2-Butene Mixtures

	Dibromide k_2		*cis* Isomer %	
Mixture	Untreated	Treated	Untreated	Treated
1	0.0523	0.0517	8.5	10.9
2	.0415	.0417	52.2	51.5

Solid Complex Salts.—Dicyclopentadiene when melted and stirred up with aqueous silver nitrate or silver perchlorate gives a white solid. The complex with silver perchlorate can be recrystallized from alcohol and dried on a porous plate but the one with silver nitrate cannot. In the absence of a solvent the silver nitrate solid can be brought to constant weight in an aspirator-evacuated desiccator containing calcium chloride and chipped paraffin. The compounds slowly darken in the light and burn somewhat explosively. Practically all of the combined hydrocarbon can be steam-distilled off easily, showing that the reaction is easily reversible. The silver nitrate compound was analyzed for silver by dissolving a weighed sample in ammonia solution, warming until the hydrocarbon was steam-distilled out, acidifying with nitric acid, adding bromide ion and weighing the silver halide. The equivalent weight found: 308, 306, average, 307; calculated for $\mathrm{AgNO_3C_{10}H_{12}}$, 302.

The silver perchlorate compound was analyzed for silver by warming slightly with water until no more solid phase was visible, acidifying with nitric acid and titrating with standard thiocyanate using ferric nitrate as the indicator. During this time there were two liquid phases. Equivalent weight found: 342, 340, average, 341; calculated for $\mathrm{AgClO_4C_{10}H_{12}}$, 339.4.

When equal volumes of biallyl and 7.5 *N* aqueous silver perchlorate are mixed, some solid is precipitated but it is very soluble, all dissolving on the addition of a volume of alcohol equal to the volume of biallyl used. No solid was obtained with equal volumes of 7.5 *N* silver perchlorate and unsaturated material in the case of 2-pentene, 1-hexene, dimethylbutadiene, trimethylethylene, propenylbenzene, pinene, allyl alcohol and crotyl alcohol.

Other Metallic Ions.—Isobutene or cyclohexene was distributed at 25 ± 5° between carbon tetrachloride and aqueous solutions of salts: cadmium nitrate, 0.8 f.; cobalt chloride, 1.0 f.; chromium sulfate, 0.5 f.; copper sulfate, 1.0 f.; ferric nitrate, 1.0 f.; lead nitrate, 1.0 f.; thallous nitrate, 0.35 f.; nickel nitrate, 1.0 f.; zinc chloride, 1.0 f. In the case of all of these salts, the olefin content of the aqueous phase was almost equal to that expected at the ionic strength existing, assuming no complex formation. In no case did the salt have so much as 2% of the salting-in effect of an equal formal concentration of silver nitrate.

Summary

A study has been made, by means of distribution measurements, of the coördination complexes which silver ion forms with (a) the monoölefins, trimethylethylene, 2-pentene, 1-hexene, cyclohexene and propenylbenzene; (b) the diolefins, dimethylbutadiene and biallyl; (c) the unsaturated oxygenated compounds, allyl alcohol, crotyl alcohol, crotonaldehyde, crotonic acid and phenol.

Complex ions of three types have been observed, *viz.*, combinations of one silver ion with one unsaturated molecule, two silver ions with one un-

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(33) Dillon, Young and Lucas, This Journal, **52**, 1953 (1930).

saturated molecule and one silver ion with two unsaturated molecules. In the case of two hydrocarbons, *viz.*, biallyl and dicyclopentadiene, solid silver complexes were obtained.

Equilibrium constants have been obtained for the reactions of silver ion with all of the unsaturated compounds mentioned (except dicyclopentadiene) at 25°, and with trimethylethylene, cyclohexene and phenol at 0°. For trimethylethylene and cyclohexene it has been found that $\Delta H = -6.0$ kcal.

Neither *cis*-2-butene nor *trans*-2-butene isomerizes in the presence of silver ion.

In aqueous solution the following ions fail to form complexes with an olefin: Cd^{++}, Co^{++}, Cr^{+++}, Cu^{++}, Fe^{+++}, Ni^{++}, Pb^{++}, Tl^{+}, Zn^{++}.

A structure is proposed for the ethylenic silver ion complex, according to which the ethylenic compound is able to occupy one of the two coördination positions of silver by acting as the donor of an electron pair. A covalence joins the silver atom to one of the two carbon atoms, and a positive charge appears on the other. Resonance involving two such bonded forms and an unbonded form is believed to account for the stability of the complex.

It is believed that many other coördination complexes have similar structures; for example, those of unsaturated compounds with platinum salts, anhydrous aluminum, ferric and zinc chlorides, iron carbonyl residues and nitro compounds. It is possible that complexes of a still lower order of stability such as those with oxygen, protons and positive bromine atoms, have similar structures.

PASADENA, CALIF.

RECEIVED NOVEMBER 29, 1937

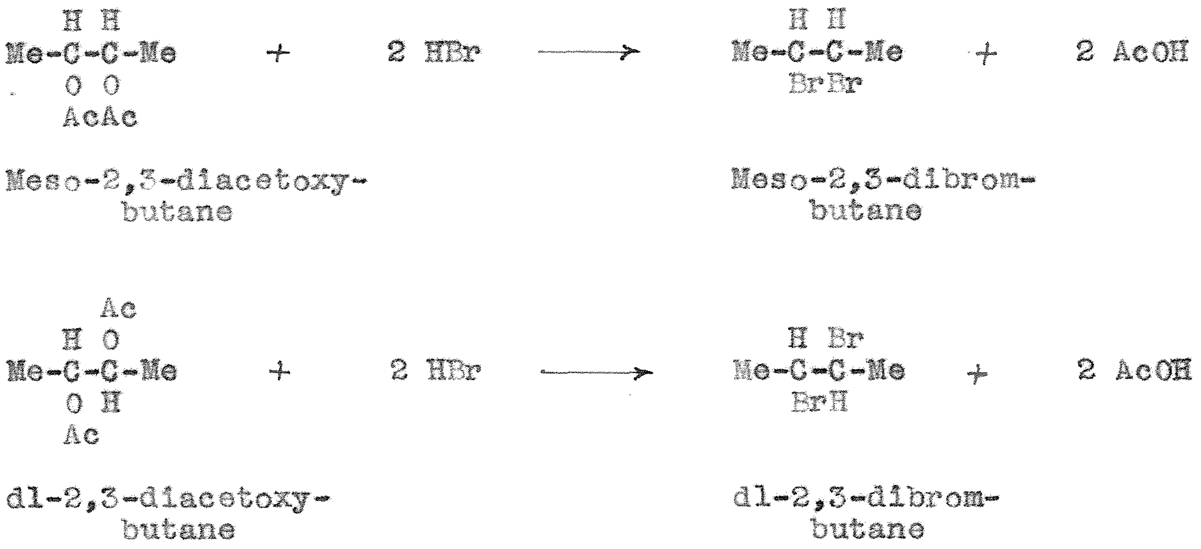
III

STEREOCHEMICAL RELATIONSHIPS IN THE CONVERSION OF ACETATES TO BROMIDES

In some transformations of butylene derivatives, Wilson and Lucas[1] found that the diacetate of meso-2,3-butandiol was converted by fuming aqueous hydrobromic acid at room temperature into a dibromide which seemed to be the racemic 2,3-dibromobutane, and that the diacetate of dl-2,3-butandiol was converted to meso-2,3-dibromobutane under the same conditions. Young, Jasaitis, and Levanas[2] obtained similar results with the 4,5-diacetoxyoctanes. The conversions were accompanied by no racemization, and the results presented a very interesting situation involving Walden inversion. The diacetates must have the same configuration as the glycols, the glycol C-O bonds not being affected. Then it appears that replacement of successive acetate groups by bromide goes differently, stereochemically speaking, in the case of the first acetate group than in the case of the second one. To put it differently, an odd number of inversions are involved in the transformation of a diacetate to a dibromide.

An apriori prediction would have been that the replacement of an acetate group by bromide with hydrobromic acid was like most replacement reactions where a negative ion replaces a negative group[3]. This would give rise to an inversion of each asymmetric carbon atom, meso-2,3-diacetoxybutane giving meso-2,3-dibromobutane. The predicted and observed reactions are shown below, Me and Ac signifying the methyl and acetyl radicals, respectively.

- Predicted Reaction -



$$\underset{\substack{O\ O\\ AcAc}}{\overset{H\ H}{Me-C-C-Me}} + 2\ HBr \longrightarrow \underset{BrBr}{\overset{H\ H}{Me-C-C-Me}} + 2\ AcOH$$

Meso-2,3-diacetoxy-butane

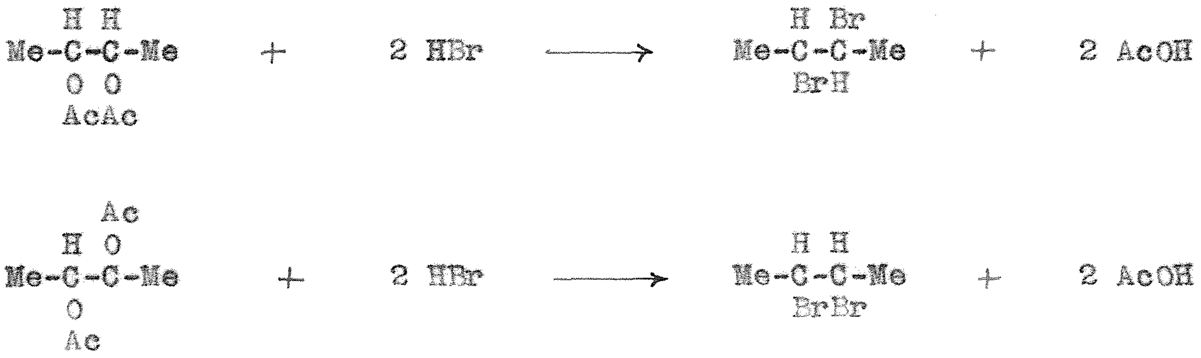
Meso-2,3-dibrom-butane

$$\underset{\substack{O\ H\\ Ac}}{\overset{\substack{Ac\\ H\ O}}{Me-C-C-Me}} + 2\ HBr \longrightarrow \underset{BrH}{\overset{H\ Br}{Me-C-C-Me}} + 2\ AcOH$$

dl-2,3-diacetoxy-butane

dl-2,3-dibrom-butane

- Observed Reaction -



$$\underset{\substack{O\ O\\ AcAc}}{\overset{H\ H}{Me-C-C-Me}} + 2\ HBr \longrightarrow \underset{BrH}{\overset{H\ Br}{Me-C-C-Me}} + 2\ AcOH$$

$$\underset{\substack{O\\ Ac}}{\overset{\substack{Ac\\ H\ O}}{Me-C-C-Me}} + 2\ HBr \longrightarrow \underset{BrBr}{\overset{H\ H}{Me-C-C-Me}} + 2\ AcOH$$

One fact that makes uncertain the interesting conclusion regarding Walden inversions in the conversion of diacetates to dibromides is that the assignment of configuration to the 2,3-dibrombutanes is based on the assumption of trans addition of bromine to the 2-butenes.

The problem seemed worthy of further investigation. If the occurrence of an odd number of inversions in the transformation of diacetoxybutane to dibromobutane were confirmed, it seemed desirable to inquire further into the situation and to apply the reaction in another connection; that is, to the transformation of trans-1,2-diacetoxycyclohexane to cis-1,2-dibromcyclohexane, a substance which should give rise to the interesting trans-cyclohexene.

Some work has now been carried out along the above lines, and although the original aims have not yet been fulfilled, the progress so far made will be reported.

A 2,3-butylene glycol was obtained from the Lucidol Corporation and was found to have optical activity. The diacetate from this glycol was, of course, optically active, but the dibromide prepared from the diacetate and hydrobromic acid had no optical activity. These results, together with the observation of Wilson and Lucas that no racemization was involved in the reaction of hydrogen bromide on the diacetate, prove conclusively that there is an odd number of inversions in the transformation of the diacetate to the dibromide. The reasoning is as follows: Laevorotatory diacetate gives an inactive dibromide. This dibromide must be the meso isomer. If it were the dl isomer or a mixture of dl and meso, then Wilson and Lucas would not have obtained two pure dibromides but only one or mixtures of the two.

Incidentally, the confirmation of the earlier conclusion serves to show that the structures of the 2,3-dibromobutanes are correctly assigned[4].

The conversion of 2,3-diacetoxybutane to dibromide was investigated under other conditions also. In acetic acid as a solvent, the reaction must be carried out at more elevated temperatures. At 100° the reaction proceeds nicely. However, inversion is not clean cut as in water. A diacetate which is 92% meso and 8% dl gives rise to a dibromide which is 32% meso and 68% dl, and which is optically inactive. This may be due to the racemizing action of hydrogen bromide on the dibromide. If this is the case, then the dibromide obtained must have the equilibrium composition since the composition did not vary with reaction time. As yet, the effect of the reaction medium on dibromobutane has not been tested.

In the attempt to prepare cis-1,2-dibromcyclohexane, the dibromide of trans-cyclohexene, trans-1,2-diacetoxycyclohexane was prepared through the series of reactions: Cyclohexanol --- cyclohexene --- 2-chlorocyclohexanol --- 1,2-epoxycyclohexane --- trans-1,2-cyclohexandiol --- trans-1,2-diacetoxycyclohexane. Unfortunately, on treatment with fuming hydrobromic acid, this diacetate did not give a layer of dibromide as the butylene and octylene glycol diacetates did. Probably the reaction would proceed in acetic acid at 100° but further work on the transformation was deferred until more was known about the diacetoxybutane-hydrogen bromide reaction in acetic acid.

In the consideration of the reaction between a glycol diacetate and hydrobromic acid the fundamental question arises as to the stereochemical course of the reaction between an acetate of a monohydric alcohol and hydrobromic acid. One such case has now been studied with rather interesting results. 2-octanol was resolved, d-octanol-2 of fairly high optical purity was converted to d-2-acetoxyoctane, which was converted to 2-bromoctane with aqueous fuming hydrobromic acid. Accepting the fact that dextrorotatory alcohol, acetate, and bromide all have the same configuration[3,5] and the estimate of 33.8° for the specific rotation of 2-bromoctane[5] and correcting the present results for the optical purity of the octanol and acetate, one obtains the result that in the conversion of 2-acetoxyoctane to 2-bromoctane with fuming hydrobromic acid there is inversion with retention of optical purity being only 67%.

The reaction between an ester and hydrobromic acid should be considered in more detail. The relatively rapid acid-catalyzed establishment of equilibrium between an ester, acid, alcohol, and water must, no doubt, take place with the production of considerable alcohol. The alcohol has the same configuration as the acetate. Then both alcohol and acetate can presumably react with hydrogen bromide to give a bromide and water or acetic acid. Depending on relative rates all the bromide may be from the reaction of the acetate or alcohol or both. Octyl alcohol and hydrogen bromide react to give a bromide having as high a specific rotation[5] as 32.5°, the rotation depending on reaction temperature. Under the conditions employed in this work, optical purity would no doubt be at least as well retained in the reaction of alcohol and hydrogen bromide. Then, from the results obtained with octyl acetate, we can say that a large portion of the octyl bromide must have arisen from reaction of acetate and hydrogen bromide, and that this reaction does not give clean cut inversion, but either gives retention of configuration with or without racemization, or inversion with racemization.

If an acetate does show a tendency toward retention of configuration in the reaction with hydrogen bromide, then in the case of a diacetate, we could imagine a mechanism whereby retention largely predominated in the replacement of the first acetate group, let us say, and inversion in the replacement of the second.

It is certain that the diacetoxybutane in going to the dibromide does not go through the glycol as an intermediate, for the glycol in fuming hydrobromic acid rearranges and gives little dibromide[1]. It is possible that hydrolysis to glycol before replacement of any acetate group with bromide accounted for the failure of diacetoxycyclohexane to give dibromcyclohexane.

In order to shed more light on the diacetoxybutane hydrobromic acid reaction, it is planned to obtain 2,3-epoxybutanes of known configuration, and to prepare 2-brom-3-acetoxybutanes of known configuration from them. The results of the action of hydrobromic acid on these 2-brom-3-acetoxybutanes should disclose whether inversion is involved in the first or second replacement of an acetate group of diacetoxybutane by bromide ion.

- EXPERIMENTAL PART -

Lucidol Butylene Glycol. - 2,3-butandiol, m. p. approximately 27°, b. p. 90° (16), rotation +0.64° in a 1 dcm. tube, was obtained from the Lucidol Corporation. The melting point of the glycol corresponds to a composition[1] of 90% meso, 10% d and l isomers.

Although in the present work, Lucidol glycol as furnished was used, a lot of 2 lbs. was recrystallized from isopropyl ether to determine the readiness of isolation of pure isomers for other work. Glycol was always recrystallized from 4 times its weight of ether. Four crystallizations gave 300 gms. of pure meso isomer, m. p. 34.2°. The glycol fractions isolated out of the several filtrates were of successively lower purity.

2,3-Diacetoxybutane. - Lucidol glycol was converted to the diacetate in 90% yield with acetic anhydride in the manner described by Wilson and Lucas[1]. Properties of the diacetate were as follows: b. p. 81.5° (11); rotation in a 1 dcm. tube -0.71°; saponification equivalent, found 87.6, calculated 87.1.

2,3-Dibromobutane. - The diacetate of Lucidol glycol with fuming hydrobromic acid gave a 93% crude yield of dibromide; n_D^{20} 1.5144; b. p. 75.2 - 75.7° (50); rotation in 1 dcm. tube 0.00°; specific reaction rate constant[6] for the reaction with potassium iodide 0.0303. Using the values[1,6] of 0.0285 for racemic dibromide and 0.0544 for the meso isomer, the obtained 2,3-dibromobutane was 93% racemic and 7% meso. This is in good agreement with the estimate of 90% meso for the composition of the original glycol.

In acetic acid as a solvent the reaction of diacetoxybutane and hydrobromic acid proceeds very slowly. Thus, 321 gms. 44% hydrogen bromide in acetic acid and 53 gms., 0.304 moles, of diacetoxybutane allowed to remain at room temperature for 3 weeks, gave on dilution with H_2O an oil which, after washing with water and sodium carbonate solution and drying with calcium chloride, gave a wide boiling range 72-89° (50) through a 15 cm. Vigreux column, no fraction of nearly correct refractive index being obtained. With shorter reaction times, the situation was similar, the products having boiling ranges and very low densities even if they were washed with concentrated sulfuric acid. Without any solvent, 0.15 moles of diacetoxybutane absorbed 0.31 moles of hydrogen bromide gas, but after 2 weeks at room temperature the reaction had not proceeded very far.

At 100° the reaction in acetic acid proceeded rapidly enough. When carried out as above described a 93% yield was obtained in 10 hours and 77% in 2 hours. The properties of the 10 hour product were as follows: n_D^{20} 1.5138; b. p. 75.0-75.9° (50); rotation in a 1 dcm. tube 0.00°; specific reaction rate constant 0.0369. The last figure gives an estimate of 68% racemic and 32% meso for the composition of the dibromide. The 2 hour product had the following properties: n_D^{20} 1.5130; b. p. 75.0-75.8° (50); rate constant 0.0352. Considering the fact that the refractive index shows the presence of an impurity, several per cent of 2-brom-3-acetoxybutane being indicated, it must be concluded that the 2 hour product is the same as the 10 hour one.

Cyclohexene. - Cyclohexanol was converted to cyclohexene (79% yield), b. p. 81.7-81.8° (760), by the Organic Syntheses method[7] except for the use of 3 times the specified quantity of concentrated sulfuric acid in order to obtain a good rate of olefin production.

Cyclohexene Oxide. - Cyclohexene chlorhydrin was prepared from 1.5 moles cyclohexene essentially according to Organic Syntheses directions[8]. Instead of steam-distilling the chlorhydrin it was extracted out with 300 mls. isopropyl ether. The ether extract was stirred with a solution of 80 gms. sodium hydroxide in 400 mls. water for 1.25 hours. Then the ether layer was distilled through 35 cms. of glass rings. Oxide, b. p. 127-129° (750), was obtained in 45% yield from the olefin.

Trans-1,2-Cyclohexandiol. - The oxide was hydrated by shaking 50 gms. with 150 gms. water containing 3 drops 60% perchloric acid. The reaction mixture warmed up and the oxide quickly went into solution. The perchloric acid was neutralized with alkali and the water was distilled off by finally decreasing the pressure to 36 mms. The solid glycol was then recrystallized from 150 mls. benzene. The yield of recrystallized material, m. p. 103.2-104.2°, was 80%.

Trans-1,2-Diacetoxycyclohexane. - The glycol was converted to the diacetate by dissolving 108 gms. of the glycol in 219 g. of acetic anhydride containing 4 drops concentrated sulfuric acid. Heat developed, the mixture was cooled a little, and the reaction was over in half an hour. Distillation through several cms. of glass rings gave a 94% yield of diacetate; b. p.

105° (4); saponification equivalent, found 100.5, calculated 100.1.

Attempted Preparation of 1,2-Dibromcyclohexane. - 221.5 gms. 40% aqueous hydrobromic acid saturated with dry hydrogen bromide at 0° and 60 gms. diacetoxycyclohexane, after standing 2 weeks at room temperature gave no oil phase but turned very black. A sample of the reaction mixture heated at 70° for 1 hour became still darker and steam distillation gave a negligible quantity of oil phase.

d-Octanol-2. - dl-octanol-2, b. p. 174-177°, was resolved by Organic Syntheses directions[9]. The crude optically active acid phthalate was not recrystallized for optical purity was not necessary. Dextrorotatory alcohol, b. p. 86.0-86.5° (20), $[\alpha]_D^{22.5}$ 8.40 calculated using known density[10], was used in the present work. Since $[\alpha]_D^{22.5}$ is 9.71 for optically pure 2-octanol[10], the octanol employed was 86.5% optically pure.

d-2-Acetoxyoctane. - Dextrorotatory 2-octanol (20 gms.) was converted to the acetate by adding 20 gms. of acetic anhydride and 3 small drops of concentrated sulfuric acid, waiting 1.5 hours, then distilling through a 15 cms. Vigreux column. Acetate, b. p. 73.5-74.4° (6), $[\alpha]_D^{22.5}$ 5.59 calculated using known density of acetate[10], and n_D^{22} 1.4139, was obtained in 87% yield. Pure d-2-acetoxyoctane[11] has $[\alpha]_D^{23}$ 6.71. Thus, the obtained acetate seems to be 83.3% optically pure. For later calculations, the mean of 83.3 and 86.5, 84.9, will be used for the optical purity.

2-Bromoctane. - 23 gms. dextrorotatory acetate was left with 160 gms. hydrobromic acid (saturated with hydrogen bromide at 0°) for 2 days with frequent shaking. The original top layer of 10.5 mms. thickness decreased to one of 5.7 mms. during the reaction period. After 2 days, the reaction vessel was opened, and a drop of the oil layer was found to have a density greater than 1.05 by comparison with aqueous solutions. This indicated essentially complete reaction. The oil layer, washed with water, twice with 10 ml. portions of concentrated sulfuric acid, then with water and potassium carbonate solutions, and dried with calcium chloride, weighed 24 gms. (94% yield). The bromide had the following properties: b. p. 79.6-80.2 (18); n_D^{23} 1.4503; $[\alpha]_D^{23}$ -19.14 calculated using the known density[10] of 2-bromoctane. The $[\alpha]_D^{23}$ would have been -22.5° if the alcohol and acetate had been optically pure.

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Thanks are due Mr. Pressman and Mr. Nicholson for services rendered during the course of this work. Mr. Nicholson prepared dl-octanol-2 and Mr. Pressman determined some of the reaction rates mentioned previously.

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Propositions For Final Examination, May 24, 1938

1. The idea of a mechanism of substitution involving attack at a carbon atom removed from the displaced group to supplement the usual mechanism of substitution involving attack on the carbon face opposite the group to be displaced is useful in explaining allylic rearrangements.

2. In calculating molecular refractions of substituted allyl bromides, $RCH=CHCH_2Br$, from atomic refractions an exaltation correction should be applied for the structure involved.

3. The finding of Schnackenberg and colleague at U.C.L.A. that one mole ascorbic acid in aqueous acid solution protected from air by carbon dioxide will use up two moles of cupric ion so that only the ascorbic acid and not the cupric ion is analyzable iodometrically and that the ascorbic acid titer then slowly drops to zero can be interpreted to indicate that the ascorbic acid molecule forms a complex with two cupric ions, the complex slowly changing to the complex of the keto-acid lactone.

4. It is doubtful whether there is much significance in the seeming agreement between the amounts of 1,2 and 1,4 addition products obtained by Young (U.C.L.A. unpublished work) and Kharasch (J. Org. Chem., <u>2</u>, 489 (1937) in the addition of hydrogen and hydrogen halides to butadiene and the contributions of resonating forms in butadiene.

5. Rothstein, (Ann. chim., <u>14</u>, 461 (1930) misinterpreted his results when he concluded that 1,2-dibromcyclohexane prepared from bromine and cyclohexene is the cis isomer.

6. In the instruction in thermodynamics or physical chemistry the

derivation of the familiar equation $\frac{W}{Q_1} = \frac{T1 - T2}{T_1}$ using a perfect gas in a Carnot cycle can be made more instructive by not making use of the previously derived expression $Tv^{\gamma - 1} = k$ and not requiring that $\frac{\partial Cv}{\partial T} = 0$.

7. In spite of complication due to side reactions, it can be concluded that both the hydration of crotonaldehyde to aldol and the reverse reaction in dilute aqueous acid solution are first order with respect to the organic compound and to the acid, and that the equilibrium constand is 0.89 at 25° and 0.64 at 35°C. J.A.C.S., <u>59</u>, 1431 (1937).

8. A general property of unsaturated molecules is the ability to form complex ions with silver ion in aqueous solution, a double bond having the ability to coordinate with one silver ion. This coordination can be explained by a structure involving resonance between three forms two of which involve a covalence between silver and a carbon atom, another carbon atom bearing a positive charge. Equilibrium constands can be interpreted in terms of steric effects and additional resonance effects. J.A.C.S., <u>60</u>, 836 (1938)

9. The conversion of meso-2,3-diacetoxybutane to dl-2,3-dibrombutane and that of dl-2,3-diacetoxybutane to meso-2,3-dibrombutane by fuming aqueous hydrobromic acid can be accounted for only by an unusual mechanism.

10. Resonance is useful in interpreting stability of oxonium compounds of organic substances, (e.g. RCHO ...HX) and of other molecular compounds.