

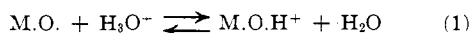
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 838]

The Hydration of Unsaturated Compounds. IX. The Oxonium Complex Constant of Mesityl Oxide^{1,2}

BY D. PRESSMAN, L. BREWER AND H. J. LUCAS

A study has been made of the coördination reaction of mesityl oxide with the hydrogen ion, since it is important to know how the oxonium complex enters into the hydration reaction of mesityl oxide.³ This was done by a study of the partition of mesityl oxide between carbon tetrachloride and various aqueous salt and acid solutions at 25 and 30°.

Oxonium Complex Constant.—The equilibrium reaction for the formation of the oxonium salt, M.O.H⁺, of mesityl oxide, M.O., is given by Eq. 1.



The equilibrium expression,⁴ $K_{\text{M.O.}}^*$, is given by Eq. 2. The activity coefficient

$$K_{\text{M.O.}}^* = \frac{(\text{M.O.H}^+)(\text{H}_2\text{O})}{(\text{M.O.})(\text{H}_3\text{O}^+)} \frac{\gamma_{\text{M.O.H}^+} \gamma_{\text{H}_2\text{O}}}{\gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+}} \quad (2)$$

product, $\gamma_{\text{M.O.H}^+} \gamma_{\text{H}_2\text{O}} / \gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+}$, is taken to have a constant value at a given ionic strength in the aqueous solutions studied.⁵ On combining this constant value with $K_{\text{M.O.}}^*$ (Eq. 2) Eq. 3 is obtained.

$$K_{\text{M.O.}} = (\text{M.O.H}^+)(\text{H}_2\text{O}) / (\text{M.O.})(\text{H}_3\text{O}^+) \quad (3)$$

The total concentration of mesityl oxide in the aqueous phase, (M.O.)_t, is the sum of the complexed and uncomplexed material, Eq. 4, and can be determined by analysis. The con-

$$(\text{M.O.})_t = (\text{M.O.H}^+) + (\text{M.O.}) \quad (4)$$

centration of the uncomplexed mesityl oxide in any aqueous solution can be calculated from the concentration of the mesityl oxide in the carbon tetrachloride phase, (M.O.)_{CCl₄}, which is in equi-

(1) Previous publication in this series, *THIS JOURNAL*, **62**, 2069 (1940).

(2) Presented at the Pasadena Meeting of the Pacific Section, Am. Assoc. Adv. Science, June 16–20, 1941.

(3) The results of the hydration studies are to be found in Part X of this series, *THIS JOURNAL*, **64**, 1122 (1942).

(4) Of course water is polymerized in aqueous solution. However, for simplicity the water is written as monomeric and the hydronium ion as H₃O⁺.

(5) Hammett and co-workers have shown that $\gamma_{\text{B}}/\gamma_{\text{BH}^+}$ is practically the same for a number of structurally similar bases of the same charge type in any given solution but is different for similar bases of a different charge type. Here γ_{B} is the activity coefficient of a base, B, and γ_{BH^+} is the activity coefficient of its conjugate acid, BH⁺. We are assuming that the activity term in Eq. 2 is a constant at any one ionic strength even though the bases are structurally different. L. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 267.

librium with the second phase, by the use of Eq. 5, where K_{D}^0 is the distribution constant of the

$$K_{\text{D}}^0 = (\text{M.O.})_{\text{CCl}_4} / (\text{M.O.})_{\text{aq}} \gamma_{\text{M.O.}}^m \quad (5)$$

uncomplexed mesityl oxide between carbon tetrachloride and pure water and $\gamma_{\text{M.O.}}^m$ is the activity coefficient of mesityl oxide in a solution of ionogen composition, m , relative to the activity coefficient in pure water taken as unity. The activity coefficient in carbon tetrachloride is taken as constant in the concentrations used. The distribution of mesityl oxide between carbon tetrachloride and water is discussed later.

The observed distribution constant, K_{D}^H , of mesityl oxide between carbon tetrachloride and an aqueous solution containing acid is given by Eq. 6.

$$K_{\text{D}}^H = (\text{M.O.})_{\text{CCl}_4} / [(\text{M.O.})_{\text{aq}} + (\text{M.O.H}^+)_{\text{aq}}] \quad (6)$$

Then

$$K_{\text{M.O.}} / (\text{H}_2\text{O}) = [K_{\text{D}}^0 \gamma_{\text{M.O.}}^m / K_{\text{D}}^H - 1] / (\text{H}_3\text{O}^+) \quad (7)$$

In order to obtain the true value of $K_{\text{M.O.}} / (\text{H}_2\text{O})$, $\gamma_{\text{M.O.}}^m$ was determined in acid solution. It was necessary to carry out the distributions with the acid solutions containing diacetone alcohol at concentrations near the hydration equilibrium concentration. Correction was made in the distribution constant for the small effect of the alcohol.

The Hydronium Ion Concentration.—It is assumed that all of the hydrogen ion (H⁺)_t is coördinated in solution according to Eq. 8

$$(\text{H}^+)_t = (\text{H}_3\text{O}^+) + (\text{M.O.H}^+) + (\text{D.A.H}^+) \quad (8)$$

An approximate value of $K_{\text{M.O.}} / (\text{H}_2\text{O})$ is obtained by using (H⁺)_t in place of (H₃O⁺) in Eq. 7 and the value of $\gamma_{\text{M.O.}}^m$ for a salt solution of ionic strength m . By means of Eq. 10, obtained by combining Eqs. 3, 8, and 9, where $K_{\text{D.A.}}$ is the oxonium complex constant for di-

$$K_{\text{D.A.}} = (\text{D.A.H}^+)(\text{H}_2\text{O}) / (\text{D.A.})(\text{H}_3\text{O}^+) \quad (9)$$

$$(\text{H}_3\text{O}^+) = (\text{H}^+)_t / \left[1 + K_{\text{M.O.}} \frac{(\text{M.O.})}{(\text{H}_2\text{O})} + K_{\text{D.A.}} \frac{(\text{D.A.})}{(\text{H}_2\text{O})} \right] \quad (10)$$

acetone alcohol, a fairly accurate value of (H₃O⁺) can be calculated, substituting for $K_{\text{M.O.}} / (\text{H}_2\text{O})$ and $K_{\text{D.A.}} / (\text{H}_2\text{O})$ the approximate value of

TABLE I
VALUES OF THE APPROXIMATE OXONIUM COMPLEX CONSTANT FOR MESITYL OXIDE, $K_{M.O.}/(H_2O)$

μ N	$(H^+)_t$ N	(M.O.) _{aq} moles/liter	(D.A.) _{aq} calcd. moles/liter	(M.O.) _{CCl₄} moles/liter	K_D^H	$K_D^O \gamma_{M.O.}^m$ (for salt)	(H ₃ O ⁺)	$\frac{(H_3O^+)}{(H^+)_t}$	$\frac{K_{M.O.}}{(H_2O)}$ 2nd approx.
HClO ₄ at 25.0°									
0.200	0.200	0.001380	0.0164	0.03335	24.2	26.8	0.198	0.991	0.56
1.00	.259	.001433	.0164	.0361	25.2	28.9	.257	.991	.58
1.02	.526	.00720	.108	.157	22.0	28.4	.505	.969	.575
1.00	.511	.00228	.035	.0515	22.6	28.8	.503	.984	.55
1.03	1.027	.00761	.111	.136	17.8	28.4	.986	.962	.60
1.00	1.000	.00443	.0641	.0827	18.7	28.7	.976	.976	.55
2.00	0.520	.00216	.0324	.0552	25.6	33.6	.511	.984	.61
2.00	1.020	.004405	.0618	.0910	20.7	33.4	.994	.975	.62
2.00	1.998	.00317	.0428	.0441	13.9	33.5	1.97	.986	.715
2.00	1.998	.00528	.0715	.0725	13.8	33.3	1.96	.979	.72
HNO ₃									
0.995	0.500	0.00735	0.106	0.181	25.1	31.8	0.481	0.962	0.555
1.00	1.002	.0074	.102	.150	20.3	32.0	.988	.950	.58
1.09	1.09	.00259	.039	.0533	20.6	33.1	1.07	.986	.565
1.90	0.191	.000903	.0164	.0326	36.1	40.7	0.189	.991	.69
2.055	1.027	.00230	.0308	.0587	25.5	42.5	1.01	.987	.66
1.91	1.907	.00493	.063	.083	16.9	40.4	1.87	.979	.745
HClO ₄ at 30.0°									
1.03	1.026	0.00870	0.102	0.1611	18.5	29.0	0.988	0.963	0.575
1.03	1.026	.00848	.100	.1560	18.4	29.0	.988	.963	.58
HNO ₃									
0.995	0.500	0.00731	0.0842	0.1862	25.5	32.7	0.485	0.969	0.58
1.00	1.001	.00544	.0638	.1176	21.6	33.1	.977	.976	.545

$K_{M.O.}/(H_2O)$ obtained above. It is shown elsewhere³ that $K_{M.O.}/(H_2O)$ and $K_{D.A.}/(H_2O)$ are nearly equal. Using this calculated value of (H_3O^+) a better approximation for $K_{M.O.}/H_3O^+$ can be obtained using Eq. 7 again.

The values of the hydronium ion concentration calculated by the use of Eq. 9 for the various concentrations of nitric and perchloric acid at different ionic strengths (regulated by their sodium salts) at 25.0° and 30.0° are in Table I. Also tabulated are K_D^H , the distribution constant involving acid solutions; $K_D^O \gamma_{M.O.}^m$, the distribution constant involving a salt solution of ionic strength, m , and containing diacetone alcohol of equilibrium concentration; $(H_3O^+)/(H^+)_t$, the fraction of total proton present as hydronium ion; and $K_{M.O.}/(H_2O)$, second approximation.

The distribution constant of mesityl oxide between carbon tetrachloride and water, K_D^O , has a constant value, 26.3, at 25° when the mesityl oxide concentration in the carbon tetrachloride is between 0.0435 and 0.1887 M but rises to 29 when the concentration in the carbon tetrachloride rises to 0.425 M , Table II. Thus at the concentrations used in the oxonium complex experiments the activity coefficient of the mesityl

TABLE II
DISTRIBUTION OF MESITYL OXIDE BETWEEN CARBON TETRACHLORIDE AND WATER; EFFECT OF DIACETONE ALCOHOL

(M.O.) _{CCl₄} moles/liter	(M.O.) _{aq} moles/liter	(D.A.) _{aq} moles/liter	K_D^O	$\Delta\%$ ^a
25°C.				
0.0435	0.00165	0.00	26.4	
.0745	.00283	.00	26.3	
.1887	.00717	.00	26.3	
.4245	.0147	.00	28.9	
.2137	.00818	.05	26.1	0.27
.1719	.00661	.06	26.0	.26
.1760	.00695	.16	25.3	.27
.0304	.00120	.25	25.3	.17
35°				
0.1417	0.00506	0.00	28.0	

^a $\Delta\%$ indicates per cent. change in K_D^O by presence of 0.01 mole of diacetone alcohol per liter of solution.

oxide in the aqueous phase is proportional to the activity coefficient in the carbon tetrachloride phase. The constant increases to 28.0 at 30°.

The effect of diacetone alcohol on the distribution constant was determined in aqueous solutions, 0.05 to 0.25 M in diacetone alcohol. The mesityl oxide distribution constant is lowered 0.25% per 0.01 mole of diacetone alcohol present per liter.

TABLE III

DISTRIBUTION OF MESITYL OXIDE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SALT SOLUTIONS

	Salt moles/liter	(M.O.)CCl ₄ moles/liter	$K_D^{m(\text{salt})}$	$\gamma_{M.O.}^{m(\text{salt})}$	s
25°					
NaClO ₄	2.03	0.0465	34.15	1.30	0.056
	1.335	.0657	30.6	1.16	.048
	1.01	.0397	29.05	1.105	.043
NaNO ₃	1.90	.0219	41.0	1.56	.101
	1.90	.0475	40.7	1.55	.100
	1.88	.02035	40.9	1.56	.102
	0.95	.0221	32.4	1.23	.095
KNO ₃	1.00	.0216	32.5	1.24	.094
NaClO ₄ } NaNO ₃ }	0.510 } .475 }	.0383	30.2	1.148	
30°					
NaClO ₄	1.013	0.1740	29.7	1.061	0.0256
NaNO ₃	1.000	.1432	33.5	1.196	.078

Effect of Salts on the Activity Coefficient of Mesityl Oxide.—The activity coefficients of mesityl oxide in sodium perchlorate, sodium nitrate and potassium nitrate solutions of various concentrations at 25° are tabulated in Table III. Sodium and potassium nitrate increase the activity coefficient of mesityl oxide to essentially the same extent, while sodium perchlorate has an appreciably smaller effect.

The relationship (11), where m is the salt concentration and s is the "salting out coefficient," a constant which is characteristic for each salt

$$(\log \gamma)/m = s \quad (11)$$

has been found to be satisfactory in describing the behavior of diacetone alcohol, benzoic acid and other compounds in salt solution, sometimes up to concentrations⁶ of 4 M . The salting out coefficients of mesityl oxide in solutions of sodium perchlorate and sodium nitrate are given in Table III. The salting out effect of sodium nitrate follows this general relationship, but that of sodium perchlorate deviates from the rule. Sodium perchlorate has much less "salting out" effect on mesityl oxide than has sodium nitrate, as is the case with the other non-electrolytes.⁷ Increasing

(6) (a) M. Randall and C. Failey, *Chem. Rev.*, **4**, 285 (1927); (b) G. Akerlof, *THIS JOURNAL*, **51**, 984 (1929); (c) E. Larsson, *Z. physik. Chem.*, **153**, 299 (1931); (d) E. Chase and M. Kilpatrick, *THIS JOURNAL*, **53**, 2594 (1931); (e) P. Gross, *Chem. Rev.*, **13**, 91 (1933).

(7) This relation holds in the case of phenylthiourea, as Randall and Failey point out.^{6a} Also, sodium nitrate has a greater salting out effect on benzoic acid than has sodium perchlorate, for from Larsson's^{6c} experimentally determined solubility data the salting out coefficients of nitrate and perchlorate ions are -0.03 and -0.06 , respectively. Unfortunately, these are erroneously tabulated as $+0.03$ and $+0.06$ respectively in his concluding table. Moreover, one gets the impression from the review paper by Gross^{6e} that per-

the temperature lowers the salting out coefficients.

Effect of a Mixture of Acid and Salt on the Activity Coefficient of Mesityl Oxide.—The salting out effect of a mixture of a salt and an acid, as for example sodium perchlorate and perchloric acid, is given by Eq. 12 where each salting out

$$\log \gamma_{M.O.}^{(\text{salt} + \text{acid})} = (\text{NaClO}_4)_{S_{\text{NaClO}_4}} + (\text{HClO}_4)_{S_{\text{HClO}_4}} \quad (12)$$

coefficient is that for a salt or acid solution whose concentration is $(\text{NaClO}_4) + (\text{HClO}_4)$.⁸ A solution 0.475 M in sodium nitrate and 0.51 M in sodium perchlorate experimentally gives a value of 1.15 for the activity coefficient of the dissolved mesityl oxide, Table III, which agrees well with the value 1.17 calculated by using the salting-out coefficients of 0.095 for 1 M sodium nitrate and 0.043 for 1 M sodium perchlorate.

Calculation of Oxonium Constant.—From Eqs. (7) and (12), $K_{M.O.}/(\text{H}_2\text{O})$ at constant ionic strength is

$$K_{M.O.}/(\text{H}_2\text{O}) = [K_D^0 10^{[(\text{salt})_{S_{\text{salt}}} + (\text{acid})_{S_{\text{acid}}}]}/K_D^H - 1]/(\text{H}_3\text{O}^+) \quad (13)$$

The small variation in $K_{M.O.}/(\text{H}_2\text{O})$ due to the difference in water concentration for nitrate and perchlorate solutions is neglected.⁹ At $\mu = 2$ there may be set up the following five equations, 14 to 18, with the three unknowns S_{HClO_4} , S_{HNO_3} , and $K_{M.O.}/(\text{H}_2\text{O})$

chlorate ion salts out more strongly than nitrate ion, because he copied Larsson's table without making correction.

The activities of benzoic acid in salt solutions as determined by W. Bosch, Thesis, University of Utrecht, 1931, are consistent with the experimental values of Larsson, according to Table II of Bosch's thesis. From Table I the opposite conclusion would be drawn, were it not for the fact that typographical errors are evident. Unfortunately, this erroneous table has been reproduced by I. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1685 (1932).

(8) See for example, S. Glasstone, D. Dimond and E. Harris, *J. Chem. Soc.*, 2938 (1926); S. Glasstone and W. Hodgson, *ibid.*, 635 (1927).

(9) Since various ions are hydrated to different extents and probably affect the extent of water polymerization differently, it is impossible at present to calculate the concentration of molecular water. It is possible to point out that the activity of water is the same (within 1%) for solutions of nitric acid, perchloric acid, hydrochloric acid, sodium chloride, sodium bromide and other salts at the same weight normality below 2 N and is very closely proportional to the mole fraction of the water present. The total water concentrations (moles H₂O/liter) in the solutions used are given below as calculated from reported density measurements.

	1 M	2 M
NaNO ₃	54.0	52.0
HNO ₃	54.0	52.1
NaClO ₄	53.0	50.4
HClO ₄	53.0	50.2

Thus the replacement of an acid by the corresponding salt at constant ionic strength does not affect the water concentration. J. N. Pearce and A. Nelson, *THIS JOURNAL*, **54**, 3544 (1932); A. Nelson, *ibid.*, **55**, 3075 (1933); F. Hartmann and P. Rosenfeld, *Z. physik. Chem.*, **A164**, 377 (1933); "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1928, Vol. 3, pp. 80, 82.

$$K_{M.O.}/(H_2O) = (0.949)10^{2.00s_{HClO_4}} - 0.509$$

$$(HClO_4, 2 N, 2\mu) \quad (14)$$

$$K_{M.O.}/(H_2O) = (1.424)10^{1.02s_{HClO_4}} - 1.006$$

$$(HClO_4, 1 N, 2\mu) \quad (15)$$

$$K_{M.O.}/(H_2O) = (2.405)10^{0.520s_{HClO_4}} - 1.961$$

$$(HClO_4, 0.5 N, 2\mu) \quad (16)$$

$$K_{M.O.}/(H_2O) = (0.821)10^{1.91s_{HNO_3}} - 0.535$$

$$(HNO_3, 2 N, 2\mu) \quad (17)$$

$$K_{M.O.}/(H_2O) = (1.297)10^{1.03s_{HNO_3}} - 0.990$$

$$(HNO_3, 1 N, 2\mu) \quad (18)$$

The distribution in 0.2 *N* perchloric acid is not included since the values of $(K_D^O \gamma_{M.O.}^m / K_D^H - 1)$ are least accurate at the low acid concentrations. An error of 1% in the distribution constant will cause an error in this function of about 3% in the 2 *N* acid solutions, 5% in the 1 *N*, 9% in the 0.5 *N* and 20% in the 0.2 *N* solutions.

The values of the three unknowns which give the best fit to the above equations were determined by systematically pairing values of s_{HClO_4} and s_{HNO_3} until a pair was obtained which gave the smallest deviation of the $K_{M.O.}/(H_2O)$ values from the mean. Figure 1 shows a set of curves which are plots of the sum of square deviations, Σr^2 , of $K_{M.O.}/(H_2O)$ values from their mean against different values of s_{HNO_3} at various constant values of s_{HClO_4} (Table IV).

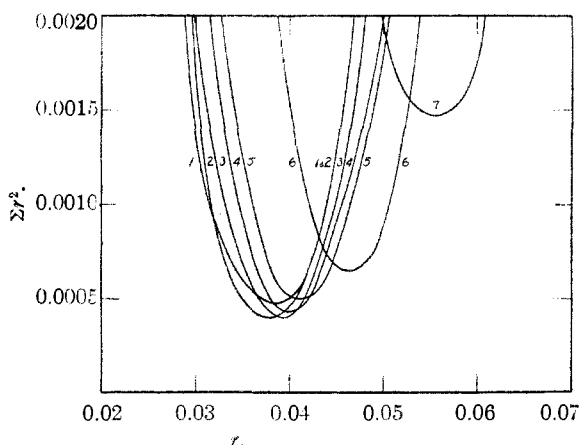


Fig. 1.—Plots of the sum of square deviations, Σr^2 , of the values of $K_{M.O.}/(H_2O)$ from the mean, against values of s_{HNO_3} at various constant values of s_{HClO_4} .

Curve	1	2	3	4	5	6	7
s_{HClO_4}	-0.001	0.000	0.001	0.002	0.003	0.009	0.020

A curve through the minima of these curves reaches a minimum value at $s_{HNO_3} = 0.040$ and $s_{HClO_4} = 0.001$. This gives $K_{M.O.}/(H_2O)$ a value of 0.44. The salting out coefficients of the acids are much less than those of the salts. Indeed the salting out effect of perchloric acid is essentially zero.

TABLE IV
MINIMA OF CURVES OF FIG. 1; BEST VALUES ARE UNDERLINED

s_{HClO_4}	s_{HNO_3} , min.	$K_{M.O.}/(H_2O)$, min.	Σr^2
-0.001	0.038	0.431	0.000479
0.000	0.038	0.433	0.000412
0.001	0.040	0.438 ^a	0.000403
0.002	0.040	0.440	0.000500
0.003	0.041	0.443	0.000510
0.005	0.041	0.447	0.000554
0.009	0.046	0.464	0.000650
0.020	0.055	0.503	0.001429

^a Probable error, ± 0.003 .

The use of the same procedure with the data at $\mu = 1$ gives $s_{HNO_3} = 0.06$, $s_{HClO_4} = 0.007$ and $K_{M.O.}/(H_2O) = 0.45$ with the deviation $\Sigma r^2 = 0.000071$. These values are really less reliable than those at $\mu = 2$, since only four equations were available in the calculation.

It is interesting to compare the basicity constant of mesityl oxide, *viz.*, 0.44, with other values: acetyl acetone,¹⁰ 0.12; acetophenone,¹¹ 9×10^{-7} ; *o*-nitraniline,¹² 1.6.

Salting Out Coefficients of Individual Ions.—

The salting out coefficients are additive for the various ions involved. Thus at $\mu = 2$ when nitrate ion replaces perchlorate ion the salting out coefficient is increased by 0.039 in the case of the acids, and by 0.044 in the case of the salts, an average of 0.04. The coefficient is increased by 0.055 when sodium replaces hydronium ion in the case of the perchlorates and by 0.060 in the case of the nitrates, an average of 0.06. The same type of additivity is valid at $\mu = 1$. The average relative salting out coefficients of the various ions for mesityl oxide are tabulated in Table V, where the coefficient of hydronium ion is taken as zero. The additivity of the ion salting out coefficients already has been pointed out in the case of benzoic acid.^{6c}

TABLE V
RELATIVE SALTING OUT COEFFICIENTS OF IONS TOWARD
MESITYL OXIDE AT 25°

	$\mu = 2$	$\mu = 1$
H_3O^+	0.000	0.000
ClO_4^-	0.001	0.007
NO_3^-	0.040	0.060
Na^+	0.057	0.035

Variation of the Activity Coefficient of the Oxonium Ion with Hydronium Ion Concentra-

- (10) F. Nachod, *Z. physik. Chem.*, **A182**, 193 (1938).
 (11) L. Flexser, L. Hammett and A. Dingwall, *THIS JOURNAL*, **57**, 2103 (1935).
 (12) L. Hammett and M. Paul, *ibid.*, **56**, 827 (1934).

TABLE VI
 VARIATION OF MEAN ACTIVITY COEFFICIENTS OF OXONIUM SALT WITH ACID CONCENTRATION

	Concn. moles/liter	$\alpha_{\text{H}_2\text{O}}$	$K_{\text{M.O.}/(\text{H}_2\text{O})}$	$\gamma_{\text{M.O.}}$	$\bar{\gamma}_{\text{H}_3\text{O}^+}$	$\frac{(\bar{\gamma}_{\text{H}_3\text{O}^+})_{2N}}{(\bar{\gamma}_{\text{H}_3\text{O}^+})_N}$	$\frac{(\bar{\gamma}_{\text{M.O.H}^+})_{2N}}{(\bar{\gamma}_{\text{M.O.H}^+})_N}$
HClO ₄	2.00	50.3	0.044	1.00	1.11	1.35	1.40
	1.00	53.4	.045	1.01	0.82		
HNO ₃	2.00	51.2	.044	1.20	.79	1.10	1.17
	1.00	53.5	.045	1.15	.72		

tion in the Absence of Added Salt.—Since the mean activity coefficient of hydronium ion and the anion, $\bar{\gamma}_{\text{H}_3\text{O}^+}$, is known for perchloric and nitric acids¹³ the ratio of the mean activity coefficient of the oxonium ion and its anion in 2 *N* acid to that in 1 *N* acid can be calculated by means of Eq. 19,

$$\frac{(\bar{\gamma}_{\text{M.O.H}^+})_{2N}}{(\bar{\gamma}_{\text{M.O.H}^+})_N} = \frac{K_{\text{M.O.}/(\text{H}_2\text{O})_{1N} (\alpha_{\text{H}_2\text{O}})_{1N} (\gamma_{\text{M.O.}})_{2N} (\bar{\gamma}_{\text{H}_3\text{O}^+})_{2N}}{K_{\text{M.O.}/(\text{H}_2\text{O})_{2N} (\alpha_{\text{H}_2\text{O}})_{2N} (\gamma_{\text{M.O.}})_{1N} (\bar{\gamma}_{\text{H}_3\text{O}^+})_{1N}} \quad (19)$$

where $\alpha_{\text{H}_2\text{O}}$ is the activity of water. This is obtained from Eq. 20 which is Eq. 2 rewritten to take into account the negative ion, for example perchlorate

$$K_{\text{M.O.}}^* = \frac{(\text{M.O.H}^+)(\text{H}_2\text{O})(\text{ClO}_4^-)(\gamma_{\text{ClO}_4^-})(\gamma_{\text{M.O.H}^+})(\gamma_{\text{H}_2\text{O}})}{(\text{H}_3\text{O}^+)(\text{M.O.})(\text{ClO}_4^-)(\gamma_{\text{ClO}_4^-})(\gamma_{\text{H}_3\text{O}^+})(\gamma_{\text{M.O.}})} \quad (20)$$

The anion concentrations cancel since only one solution is involved. The activity coefficients of the anions are not cancelled since their products with the coefficients of the corresponding cations are the squares of the mean activity coefficient which are determined experimentally. Since $K_{\text{M.O.}}^*$ is constant, the ratio of the expressions for one and two normal acids yields Eq. 19. The values of the ratios are in Table VI. It is very interesting that the ratios $(\gamma_{\text{M.O.H}^+})_{2N}/(\gamma_{\text{M.O.H}^+})_{1N}$ and $(\bar{\gamma}_{\text{H}_3\text{O}^+})_{2N}/(\bar{\gamma}_{\text{H}_3\text{O}^+})_{1N}$ are approximately the same for solutions of any one acid.

Thermochemistry.—The apparent heat of oxonium complex formation from hydronium ion and aqueous mesityl oxide according to Eq. 1 is essentially zero since the approximate value of $K_{\text{M.O.}/(\text{H}_2\text{O})}$ in Table I does not change with temperature in the range 25 to 30°.

The heat of distribution of mesityl oxide from carbon tetrachloride to dilute aqueous solution is 2.19 ± 0.15 kcal. for pure water, 0.79 ± 0.15 kcal. for 1 *N* sodium perchlorate solution, and 0.76 ± 0.15 kcal. for 1 *N* sodium nitrate solution. From these values, it is evident that 1.4 kcal. is evolved when a mole of mesityl oxide is transferred from 1 *N* salt solution to pure water.

(13) Landolt-Börnstein, "Phys.-chem. Tabellen," Julius Springer, Berlin, 1936, 5th edition, vol. 3, pt. 3, p. 2144.

Experimental

Materials.—Eastman Kodak Co. mesityl oxide was twice fractionated and the almost colorless portion, b. p. 48–49° (39–40 mm.), was used immediately for preparing 0.025 and 0.05 *M* aqueous solutions. On standing, pure mesityl oxide becomes yellow. When potassium iodide is added to mesityl oxide which has stood for several days, iodine color develops. This indicates the formation of a peroxide, from absorption of oxygen. The aqueous solutions did not absorb oxygen. Since the solubility of mesityl oxide is only 0.30 molal at 25°, the vapor pressure is high and care was taken to avoid errors due to evaporation of the mesityl oxide.

Eastman Kodak Co. diacetone alcohol was fractionated and the middle portion, b. p. 71–72° (23–24 mm.), was used. This contained less than 0.01% mesityl oxide as determined by bromine absorption.

The inorganic chemicals were of c. p. grade. The nitric acid gave no test for nitrogen oxides with potassium iodide. The standard salt solutions were prepared by the neutralization of standard acid solutions or by weighing out the dried salt. The carbon tetrachloride was treated with chlorine in sunlight, washed with alkali, and fractionated.

Analysis.—The mesityl oxide was determined by a bromine absorption method similar to that used previously.¹⁴ Bromine was taken up by the mesityl oxide as fast as it was liberated by the bromate–bromide solution and the bromination was complete by the time of the appearance of the yellow color due to excess bromine.

Since mesityl oxide dibromide and diacetone alcohol are methyl ketones, substitution by iodine takes place rapidly in 1 *N* acid. However, as noted by Dawson and Key¹⁵ in the case of mesityl oxide and by Zucker and Hammett¹⁶ in the case of acetophenone, the reverse reaction of the iodo compound with iodide ion also is catalyzed by hydrogen ion and equilibrium is reached in less than two minutes with only 1 to 2% substitution. During the titration of the iodine by thiosulfate solution, the substitution reverses and practically all of the iodine is liberated during the time of titration if the acid concentration at the end-point is at least 1 *N*. In the titration of the carbon tetrachloride samples, the procedure was modified by shaking for one minute during the bromination since bromination in the carbon tetrachloride phase was much slower than in the aqueous phase.

Procedure for Distribution Experiments.—The mesityl oxide was distributed between water and carbon tetrachloride by vigorous shakings of the two phase system in a thermostat at 25.00 ± 0.01°. Equilibrium was rapidly reached as shown by the fact that further shaking

(14) S. Winstein and H. J. Lucas, *THIS JOURNAL*, **59**, 1461 (1937).

(15) H. Dawson and A. Key, *J. Chem. Soc.*, 2154 (1928).

(16) L. Zucker and L. P. Hammett, *THIS JOURNAL*, **61**, 2791 (1939).

did not change the mesityl oxide concentration. The distribution constant was determined by analysis of portions taken from each phase. Sampling was carried out by the use of a special stopcock pipet which was calibrated to contain a definite volume.¹⁷

Summary

The oxonium complex constant (basicity constant) for mesityl oxide, $K_{M.O.}/(H_2O)$, was investigated by a distribution method at 25° and found to be 0.44 and 0.45 in aqueous solutions of ionic strengths two and one, respectively.

The distribution constant of mesityl oxide between carbon tetrachloride and water is a constant, 26.3, at 25° when the mesityl oxide concentration in carbon tetrachloride is 0.2 *M* or lower. The value increases to 28.0 at 30°. Diacetone

(17) W. Eberz and H. J. Lucas, *THIS JOURNAL*, **56**, 1230 (1934).

alcohol lowers the value 0.25% per 0.01 mole present per liter of aqueous phase.

The additive relative salting out coefficients of the ions, H_3O^+ , ClO_4^- , NO_3^- and Na^+ on mesityl oxide at 25° are 0.000, 0.001, 0.040 and 0.057, respectively, at ionic strength two, and 0.000, 0.007, 0.060 and 0.035 at ionic strength one.

The variation of the square mean activity coefficient of mesityl oxide oxonium ion with acidity is proportional to the variation of the square mean activity coefficient of hydronium ion.

The apparent heat of oxonium complex formation from aqueous mesityl oxide and hydronium ion is essentially zero.

The heat of transference of a mole of mesityl oxide from *N* salt solution to pure water is 1.4 kcal.

PASADENA, CALIFORNIA

RECEIVED JULY 7, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 839]

The Hydration of Unsaturated Compounds. X. The Role of the Oxonium Complexes in the Hydration of Mesityl Oxide and the Dehydration of Diacetone Alcohol¹

BY D. PRESSMAN, L. BREWER AND H. J. LUCAS

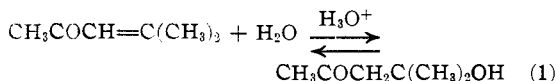
In connection with the acid catalyzed hydration of an unsaturated compound containing oxygen,² it is important to know how the coordination reaction between the oxygen atom and a proton influences the course of the hydration.

In the case of mesityl oxide the oxonium complex constant has been determined.³ The problem was then undertaken to determine the effect of aqueous perchloric acid and nitric acid solutions of various hydrogen ion concentrations and ionic strengths on the hydration of mesityl oxide, the dehydration of diacetone alcohol and the equilibrium between the two.

The equilibrium between mesityl oxide and diacetone alcohol is undisturbed by side reactions.⁴ From the shift in equilibrium at constant ionic strength with change in concentration of acid, the oxonium complex constant for diacetone alcohol can be calculated. Knowing the oxonium complex constant for mesityl oxide and for diac-

etone alcohol, the relative rates of the complexed and uncomplexed compounds in hydration and dehydration, respectively, can be calculated.

The Rate of Hydration of Mesityl Oxide; the Rate of Dehydration of Diacetone Alcohol; Effects of Hydrogen Ion Concentration and Ionic Strength.—The two opposing reactions take place in dilute aqueous acid solution



and can be followed quantitatively by bromination.

Both forward and reverse reactions are first order with respect to the organic reactant, since Eq. 2 holds

$$(k_1 + k_{-1})t = 2.303 \log_{10} \epsilon / (\epsilon - x) \quad (2)$$

where x and ϵ are the fractions of organic material converted at the time, t , and at equilibrium, respectively, and k_1 and k_{-1} are the specific reaction rate constants for the hydration and dehydration reactions, respectively. This is shown by the straight line character of the plot of $\log_{10} (\epsilon - x)$ against time where the starting material is either mesityl oxide or diacetone alcohol (Fig. 1). The

(1) Presented at the Pasadena Meeting of the Pacific Section, Am. Assoc. Adv. Science, June 16–20, 1941.

(2) (a) S. Winstein and H. J. Lucas, *THIS JOURNAL*, **59**, 1461 (1937); (b) D. Pressman and H. J. Lucas, *ibid.*, **61**, 2271 (1939); (c) D. Pressman and H. J. Lucas, *ibid.*, **62**, 2069 (1940).

(3) D. Pressman, L. Brewer and H. J. Lucas, *ibid.*, **64**, 1117 (1942).

(4) A. Hoffman [*ibid.*, **49**, 530 (1927)] has shown that the hydration of mesityl oxide is reversible.