

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

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.

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

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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

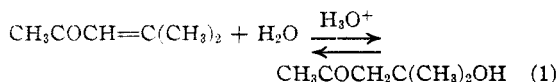
In connection with the acid catalyzed hydration of an unsaturated compound containing oxygen,² it is important to know how the coordination reaction between the oxygen atom and a proton influences the course of the hydration.

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.

TABLE I

SPECIFIC REACTION RATE CONSTANTS FOR THE HYDRATION OF MESITYL OXIDE AND THE DEHYDRATION OF DIACETONE ALCOHOL AT 25.0°

	$\frac{\mu}{N}$	$(H^+)_t$ N	(M.O.) M	(H_2O^+) M	ϵ observed	$k_1 + k_{-1}$, hr. ⁻¹	k_1 , hr. ⁻¹	k_{-1} , hr. ⁻¹	$\frac{k_1}{(H^+)_t}$	$\frac{k_{-1}}{(H^+)_t}$	$\frac{k_1}{(H_2O^+)}$	$\frac{k_{-1}}{(H_2O^+)}$	(M.O.) (M.O.) _t	(D.A.) (D.A.) _t
HClO ₄	0.20	0.1994	0.0128	0.198	0.942	0.0579	0.0545	0.0034	0.274	0.0168	0.275	0.0172		
	1.01	0.1995	.0128	.1983	.939	.0691	.0649	.0042	.325	.0211	.327	.0212	0.92	0.94
	1.00	0.510	.0126	.507	.938	.1665	.1562	.0103	.306	.0202	.308	.0203	.81	.86
	1.00	1.000	.0126	.994	.9355	.304	.284	.0196	.284	.0196	.286	.0197	.69	.77
	1.00	1.000	.0244 ^a	.988	.936	.302	.282	.0193	.282	.0193	.286	.0195	.69	.77
	2.00	0.520	.0126	.517	.937	.205	.192	.0129	.369	.0248	.371	.0250	.81	.85
	2.00	1.020	.0126	1.014	.933	.382	.356	.0256	.349	.0251	.351	.0252	.69	.75
	2.00	1.020	.0247	1.008	.929	.375	.348	.0266	.341	.0261	.346	.0264	.69	.75
	2.00	1.998	.0126	1.987	.930	.686	.639	.0473	.320	.0237	.322	.0238	.53	.60
	2.03	2.025	.0244	2.003	.933	.691	.645	.0463	.318	.0229	.322	.0231	.53	.60
HNO ₃	0.25	0.2490	.0127	0.248	.942	.0755	.0711	.00437	.286	.0176	.287	.0176		
	0.50	0.5022	.0127	.499	.939	.144	.135	.0088	.269	.0175	.270	.0176		
	1.005	0.4990	.0126	.496	.935	.155	.145	.0101	.291	.0202	.292	.0203	.82	.87
	1.00	1.002	.01155	.997	.933	.274	.256	.0184	.256	.0184	.257	.0185	.69	.78
	2.01	0.4980	.0126	.495	.932	.193	.180	.0131	.362	.0263	.364	.0265	.82	.86
	2.01	1.006	.0125	1.000	.930	.352	.327	.0246	.325	.0245	.327	.0246	.69	.75
	2.02	2.016	.01155	2.003	.927	.615	.570	.0449	.284	.0223	.284	.0224	.53	.60

^a Initial concentrations, mesityl oxide, 0.0000, diacetone alcohol, 0.0244 *M*.

values for k_1 and k_{-1} were calculated from the slope $(k_1 + k_{-1})/2.303$, taken from plots of the type of Fig. 1 and the equilibrium constant.

Table I shows the calculated values of k_1 , k_{-1} , $k_1/(H^+)_t$, $k_{-1}/(H^+)_t$ and ϵ . The values of the two quotients $k_1/(H^+)_t$ and $k_{-1}/(H^+)_t$ decrease with increasing hydrogen ion concentration at constant ionic strength. If the reaction were second order with respect to the total hydrogen ion concentration, an opposite effect would be expected. The variation in the values of the quotients at constant ionic strength is greater for nitric than for perchloric acid. At constant hydrogen ion concentration, the rate constants decrease with decreasing ionic strength. Doubling the concentration of organic material has only a slight effect on the specific rate constants.

The Equilibrium between Mesityl Oxide and Diacetone Alcohol: Effect of Hydrogen Ion Concentration and Ionic Strength.—Since the equilibrium is far to the side of diacetone alcohol, the equilibrium constants were determined independently of the rate experiments, in order to avoid any cumulative evaporation losses which might arise from the successive sampling in the rate experiments. The equilibrium was approached from both sides. The solutions were allowed to stand for some time afterward, with no significant change taking place. The results are shown in Table II. The constancy of the equilibrium is shown, for example, in 1 *N* nitric acid where the mixture reached equilibrium within eighty hours and then stood twenty-two days without appreciable change. When the equilibrium was approached from the diacetone alcohol

side the value of the equilibrium constant K_E was about 1% lower than the value obtained when mesityl oxide was the starting material. Probably this was due to the much lower volatility of diacetone alcohol. The value of K_E is independent of the concentration of the organic material. It decreases when the ionic strength at constant hydrogen ion concentration increases.

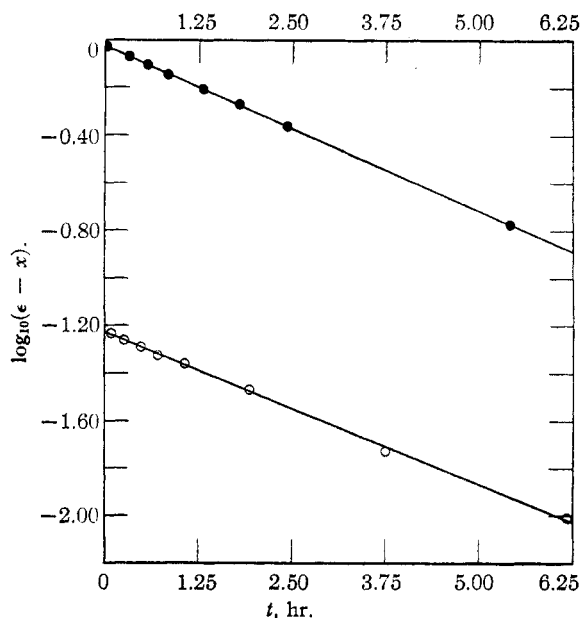


Fig. 1.—Plot of $\log_{10}(\epsilon - x)$ against time for the hydration of mesityl oxide and the dehydration of diacetone alcohol at 25.0° in *N* perchloric acid: ○, hydration; ●, dehydration.

Oxonium Complex Constant of Diacetone Alcohol, $K_{D.A.}$ —This, Eq. 3, has the form of the

TABLE II
 EQUILIBRIUM CONSTANT FOR THE HYDRATION OF MESITYL OXIDE AT 25°

	μ N	(H ⁺) _t N	Starting compd.	(D.A. + M.O.), moles/liter	K_E	Probable error of mean	Detns.	Time range of detns., hr.
HClO ₄	2.0	2.00	M.O.	0.025	13.7	0.1	5	17 to 120
	2.0	2.00	M.O.	.013	13.3	.1	2	18 to 30
	2.0	2.00	D.A.	.024	13.55	.05	6	120 to 164
	2.0	1.00	M.O.	.025	14.2 ^a	.1	5	48 to 120
	2.0	1.00	D.A.	.024	14.0	.1	4	120 to 164
	2.0	0.50	D.A.	.024	14.8	.1	4	120 to 164
	1.0	1.00	M.O.	.025	14.9	.05	4	48 to 134
	1.0	1.00	D.A.	.024	14.5	.05	3	12 to 24
	1.0	0.50	D.A.	.024	15.0	.075	3	120 to 164
	1.0	.20	M.O.	.013	15.2	.05	3	120 to 145
	0.8	.20	D.A.	.024	15.8	.1	3	120 to 145
	.5	.50	M.O.	.025	15.7	.1	3	48 to 158
	.5	.50	D.A.	.024	15.5	.1	3	120 to 160
	.2	.20	M.O.	.013	16.1	.3	4	120 to 150
	.2	.20	D.A.	.024	16.3	.05	4	120 to 160
HNO ₃	2.0	2.00	M.O.	.013	12.8	.1	4	80 to 110
	1.9	1.91	D.A.	.024	13.1	.2	2	120 to 164
	2.0	1.00	M.O.	.013	13.3	.1	7	80 to 150
	2.0	0.50	M.O.	.013	13.9	.2	4	80 to 650
	1.0	1.00	M.O.	.013	13.7	.15	3	80 to 600
	1.0	0.50	M.O.	.013	14.4	.05	2	27 to 72
	0.5	.50	M.O.	.013	15.4	.2	2	80 to 150
	.25	.25	M.O.	.013	16.2	.1	4	140 to 250

^a 13.1 in 17 hours.

mesityl oxide constant, $K_{M.O.}$ (Eq. 4), as shown previously.³

$$K_{D.A.}/(H_2O) = (D.A.H^+)/[(D.A.)(H_3O^+)] \quad (3)$$

$$K_{M.O.}/(H_2O) = (M.O.H^+)/[(M.O.)(H_3O^+)] \quad (4)$$

The value⁵ of $K_{D.A.}/(H_2O)$ can be calculated from the known value of $K_{M.O.}/(H_2O)$ and the observed hydration equilibrium constant, K_E , by the use of Eq. 5. This equation has two un-

$$K_E = \frac{(D.A.)_t}{(M.O.)_t} = \frac{(D.A.) + (D.A.)(H_3O^+)K_{D.A.}/(H_2O)}{(M.O.) + (M.O.)(H_3O^+)K_{M.O.}/(H_2O)} = \frac{[1 + K_{D.A.}(H_3O^+)/[(H_2O)](D.A.)]}{[1 + K_{M.O.}(H_3O^+)/[(H_2O)](M.O.)]} \quad (5)$$

known constants at constant ionic strength, *viz.*, $K_{D.A.}/(H_2O)$ and $(D.A.)/(M.O.)$.^{6,7} The best

(5) It will be shown later that the value of $K_{D.A.}$ calculated from this expression probably is only for the case where the proton is coordinated at the carbonyl oxygen. When it is coordinated at the hydroxyl oxygen the diacetone alcohol may dehydrate without catalysis and this reaction cannot be distinguished from and probably is the same as the hydronium ion catalyzed dehydration of uncomplexed diacetone alcohol.

(6) The value of the hydronium ion concentration was calculated from Eq. 10.

(7) The true equilibrium constant, K_E^0 , between uncomplexed mesityl oxide and uncomplexed diacetone alcohol is given by Eq. 6

$$K_E^0 = \frac{(D.A.)}{(M.O.)(H_2O)} \frac{\gamma_{D.A.}}{\gamma_{M.O.} \gamma_{H_2O}} \quad (6)$$

The activity of water is practically constant in the different solutions of constant ionic strength since the ionogens are all of the univalent-univalent type.⁸ Likewise, the activity coefficients of diacetone alcohol and mesityl oxide can be assumed to be affected proportionately by replacement of one salt or acid by another. Thus at constant ionic strength the ratio $\gamma_{D.A.}/\gamma_{M.O.}$ can be regarded as essentially constant, and therefore the ratio $(D.A.)/(M.O.)$ is a constant at equilibrium.

values of $K_{D.A.}/(H_2O)$ and $(D.A.)/(M.O.)$ at constant ionic strength were obtained by least square calculations from the several values of K_E at that ionic strength, and are in Table III.

 TABLE III
 OXONIUM COMPLEX CONSTANT FOR DIACETONE ALCOHOL
 AT 25°

μ , N	$K_{M.O.}$ (H ₂ O)	$K_{D.A.}/(H_2O)$	$(D.A.)$ (M.O.)	$(D.A.H^+)$ (M.O.H ⁺)
1	0.45	0.30 ± 0.05	15.8 ± 0.5	10.5
2	.44	.33 ± .05	14.9 ± .5	11.2

It is surprising that the values of $K_{D.A.}/(H_2O)$ are so close to the values of $K_{M.O.}/(H_2O)$ since it would be expected that the basic character of mesityl oxide would be enhanced by the conjugated system, and that the basic character of diacetone alcohol would be depressed by the possibility of hydrogen bonding between the two oxygen atoms.

Role of Oxonium Salts in the Hydration of Mesityl Oxide and the Dehydration of Diacetone Alcohol.—When mesityl oxide hydrates, presumably the uncomplexed form can react, since isobutylene⁸ and trimethylethylene⁹ hydrate in dilute aqueous acid. The reaction is taken to be first order with respect to the uncomplexed mesityl oxide and also hydronium ion. Thus

(8) H. J. Lucas and W. F. Eberz, *This Journal*, **56**, 466 (1934).

(9) H. J. Lucas and V. Liu, *ibid.*, **60**, 2138 (1934).

$$-\frac{d(\text{M.O.})}{dt} = k_1^{*'} (\text{M.O.})(\text{H}_3\text{O}^+) \gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{M.O.} \cdot \text{H}_3\text{O}^+} \quad (7)$$

where $\text{M.O.} \cdot \text{H}_3\text{O}^+$ is the Brönsted type intermediate complex in the hydration. Since $\gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{M.O.} \cdot \text{H}_3\text{O}^+}$ is a constant as the hydronium ion is increased at constant ionic strength (shown later), the observed increase in $k_1/(\text{H}_3\text{O}^+)$ at constant ionic strength with increase in (H_3O^+) , Table I, must be due to the hydronium ion catalyzed hydration of the oxonium salt which is present. Thus the hydration of mesityl oxide involves a hydronium ion catalyzed hydration of both uncomplexed and complexed mesityl oxide. The reactive intermediate complex between mesityl oxide and a proton in the hydration of uncomplexed mesityl oxide must be different from the stable oxonium complex in which the proton is attached to the carbonyl oxygen and is not available for coordination with the double bond.

Similarly both the uncomplexed and complexed diacetone alcohol undergo dehydration catalyzed by hydronium ion. It is not possible to differentiate between the spontaneous dehydration of any complexed diacetone alcohol with the proton on the hydroxyl group, and the hydronium ion catalyzed dehydration of uncomplexed diacetone alcohol, since both of these dehydrations appear as first order with respect to hydronium ion and to diacetone alcohol. Probably the same mechanism holds for both reactions.

In the stable oxonium complex of diacetone alcohol which undergoes dehydration by a hydronium ion catalyzed reaction, the proton probably is coordinated with the carbonyl oxygen atom. Since the variation of K_E with the hydronium ion concentration at constant ionic strength is also due to this oxonium complex, the observed equilibrium constant for the formation of the oxonium complex of diacetone alcohol, *viz.*, $K_{\text{D.A.}} = 0.3$, probably is concerned mainly with $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{C}(\text{CH}_3)=\text{O} \cdot \text{H}^+$.

Specific Reaction Rate Constants for Complexed and Uncomplexed Species, in Hydration and Dehydration.—The rate expression for the disappearance of mesityl oxide in a hydration experiment, where the activity coefficients in the denominator are for the Brönsted type intermediate complexes, is given by Eq. 8

$$-\frac{d(\text{M.O.})}{dt} = \left[k_1^{*'} (\text{M.O.}) \frac{\gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+}}{\gamma_{\text{M.O.} \cdot \text{H}_3\text{O}^+}} + k_1^{*''} (\text{M.O.} \cdot \text{H}^+) \frac{\gamma_{\text{M.O.} \cdot \text{H}^+} \gamma_{\text{H}_3\text{O}^+}}{\gamma_{\text{M.O.} \cdot \text{H}^+ \cdot \text{H}_3\text{O}^+}} \right] (\text{H}_3\text{O}^+) \quad (8)$$

$$k_{-1}^{*'} (\text{D.A.}) \frac{\gamma_{\text{D.A.}} \gamma_{\text{H}_3\text{O}^+}}{\gamma_{\text{D.A.} \cdot \text{H}_3\text{O}^+}} - k_{-1}^{*''} (\text{D.A.} \cdot \text{H}^+) \frac{\gamma_{\text{D.A.} \cdot \text{H}^+} \gamma_{\text{H}_3\text{O}^+}}{\gamma_{\text{D.A.} \cdot \text{H}^+ \cdot \text{H}_3\text{O}^+}} \quad (9)$$

which reduces to Eq. 9

$$-\frac{d(\text{M.O.})}{dt} = \{ [k_1' + k_1'' (\text{H}_3\text{O}^+)] (\text{M.O.}) - [k_{-1}' + k_{-1}'' (\text{H}_3\text{O}^+)] (\text{D.A.}) \} (\text{H}_3\text{O}^+) \quad (9)$$

where k_1' is $k_1^{*'} (\gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{M.O.} \cdot \text{H}_3\text{O}^+})$, k_1'' is $k_1^{*''} (K_{\text{M.O.}} \gamma_{\text{M.O.} \cdot \text{H}^+} \gamma_{\text{H}_3\text{O}^+} / (\text{H}_2\text{O}) \gamma_{\text{M.O.} \cdot \text{H}^+ \cdot \text{H}_3\text{O}^+})$, and similar terms hold for k_{-1}' and k_{-1}'' . Experimentally determined k_1 and k_{-1} are equal, respectively, to $(\text{H}_3\text{O}^+) [k_1' + k_1'' (\text{H}_3\text{O}^+)] / [1 + K_{\text{M.O.}} (\text{H}_3\text{O}^+) / (\text{H}_2\text{O})]$ and $(\text{H}_3\text{O}^+) [k_{-1}' + k_{-1}'' (\text{H}_3\text{O}^+)] / [1 + K_{\text{D.A.}} (\text{H}_3\text{O}^+) / (\text{H}_2\text{O})]$.

The hydronium ion concentration is calculated by Eq. 10 and changes less than 0.1% during any one run.

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

The values of k_1' and k_{-1}' can be found by extrapolation of plots of $k_1[1 + K_{\text{M.O.}} (\text{H}_3\text{O}^+) / (\text{H}_2\text{O})] / (\text{H}_3\text{O}^+)$ and $k_{-1}[1 + K_{\text{D.A.}} (\text{H}_3\text{O}^+) / (\text{H}_2\text{O})] / (\text{H}_3\text{O}^+)$ against (H_3O^+) to zero hydronium ion concentration, Fig. 2. It is significant that practically the same value is obtained for k_1' in nitrate solutions and perchlorate solutions at constant ionic strength. (The values of k_{-1} are not accurate enough to show this clearly.) This indicates that the activity coefficient term, $\gamma_{\text{M.O.}} \gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{M.O.} \cdot \text{H}_3\text{O}^+}$, is the same in nitrate and perchlorate solutions, even though it has been shown that $\gamma_{\text{M.O.}}$ varies for the two solutions.³ This is what might be expected since the complex has the properties of both the organic compound and hydronium ion. Thus the replacement of sodium ion by hydronium ion probably does not affect the constancy of the activity coefficient term, just as was assumed previously. This is borne out by the facts that the hydration rate constants of isobutylene⁸ and trimethylethylene,⁹ which are not known to complex appreciably with hydronium ion, are constant at constant ionic strength.

The straight line character of the curves for the hydration, the slopes of which are k_1'' and equal to $k_1^{*''} (K_{\text{M.O.}} \gamma_{\text{M.O.} \cdot \text{H}^+} \gamma_{\text{H}_3\text{O}^+} / (\text{H}_2\text{O}) \gamma_{\text{M.O.} \cdot \text{H}^+ \cdot \text{H}_3\text{O}^+})$ shows that $\gamma_{\text{M.O.} \cdot \text{H}^+} \gamma_{\text{H}_3\text{O}^+} / \gamma_{\text{M.O.} \cdot \text{H}^+ \cdot \text{H}_3\text{O}^+}$ for the oxonium ion is also independent of the replacement of hydronium ion by sodium ion. However, replacing nitrate ion by perchlorate ion increases the slope, and therefore the value of the activity coefficient

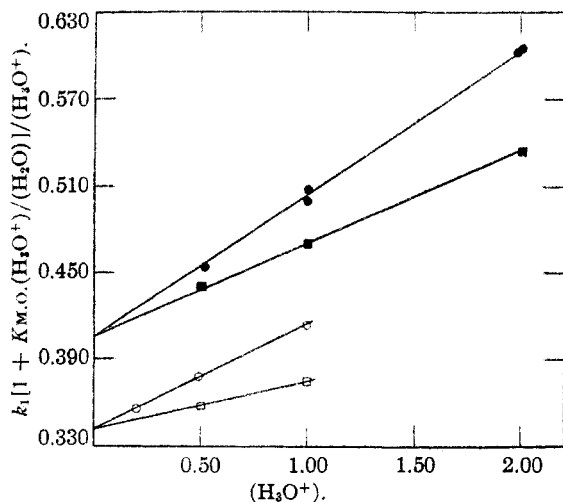


Fig. 2A.—Plot of $k_1[1 + K_{M.O.}(H_3O^+)/ (H_2O)] / (H_3O^+)$ against (H_3O^+) at 25° : ●, perchloric acid at $\mu = 2$; ○, perchloric acid at $\mu = 1$; ■, nitric acid at $\mu = 2$; □, nitric acid at $\mu = 1$.

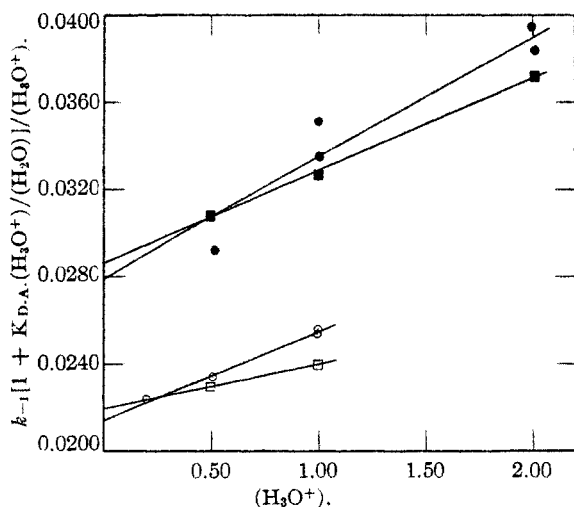


Fig. 2B.—Plot of $k_{-1}[1 + K_{D.A.}(H_3O^+)/ (H_2O)] / (H_3O^+)$ against (H_3O^+) at 25° : ●, perchloric acid at $\mu = 2$; ○, perchloric acid at $\mu = 1$; ■, nitric acid at $\mu = 2$; □, nitric acid at $\mu = 1$.

term. This is what might be expected since this term concerns ions of two charge types and it is probable that the activity of a positive ion is affected more by a variation in the negative ions present than in the variation of another positive ion.

The curves for the dehydration are not as satisfactory as those for the hydration since the experimental errors in the former are much greater due to the fact that the equilibrium lies so far on the diacetone alcohol side.

The values of the rate constants, k'_1 and $k'_{1, \text{oxonium}}$ (the latter is equal to $k'_1 \gamma_{M.O.H} \gamma_{H_3O^+} /$

$\gamma_{M.O.H+H_3O^+}$), as calculated by means of the method of least squares for the uncomplexed and complexed compounds are listed in Table IV.

TABLE IV
SPECIFIC REACTION RATE CONSTANTS FOR COMPLEXED AND UNCOMPLEXED MOLECULES AT 25°

Acid	μ, N	$k'_1, \text{hr.}^{-1}$	$k'_{1, \text{oxonium}}, \text{hr.}^{-1}$	$k'_{-1}, \text{hr.}^{-1}$	$k'_{-1, \text{oxonium}}, \text{hr.}^{-1}$
HClO ₄	2.00	0.400	0.23	0.0275	0.0185
	1.00	.336	.17	.0215	.013
HNO ₃	2.00	.410	.141	.0286	.0087
	1.00	.342	.067	.0228	.004

Figure 3 contains plots of the fraction of the total hydration due to mesityl oxide oxonium complex, $k'_1(H_3O^+) / [k'_1 + k'_{1, \text{oxonium}}(H_3O^+)]$, against the hydronium ion concentration at constant ionic strength: also the corresponding values in the dehydration of diacetone alcohol.

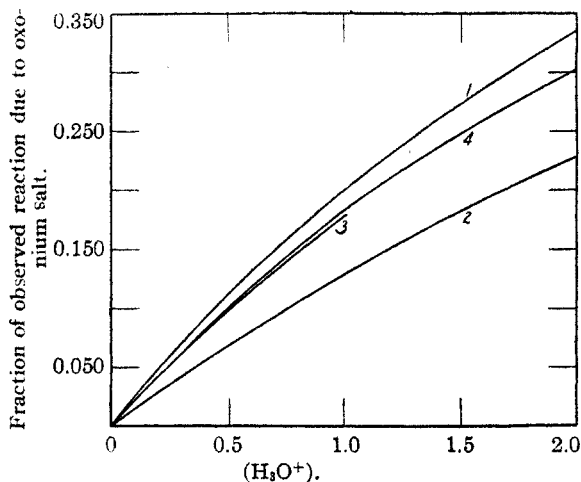


Fig. 3.—Plots of the fraction of the observed hydration and dehydration reactions due to the oxonium salts against (H_3O^+) : 1, hydration in 2 *N* perchloric acid; 2, hydration in 2 *N* nitric acid; 3, hydration in *N* perchloric acid; 4, dehydration in 2 *N* perchloric acid.

Thermal Constants

The values of the various constants determined for the reaction rates and equilibria at various temperatures are listed in Table V.

The heats of activation, Table VI, were obtained from the slopes of plots of the logarithm of $k/(H^+)_t$ against the reciprocal of the absolute temperature, $1/T$, Fig. 4. Good straight line curves were obtained in all cases for points at 35° and lower. The point for k_1 at 45° in perchloric acid deviates, due probably to evaporation losses.

The heat of activation is not influenced appreciably by the nature of the solution. The average value for hydration is 12.8 ± 0.15 and for

TABLE V
RATE CONSTANTS FOR THE HYDRATION OF MESITYL OXIDE AND THE DEHYDRATION OF DIACETONE ALCOHOL AT VARIOUS TEMPERATURES

μ	(H ⁺)	ϵ	K_E	Temp., °C.	$k_1 + k_{-1}$, hr. ⁻¹	k_1 , hr. ⁻¹	k_{-1} , hr. ⁻¹	$k_1/(H^+)_t$	$k_{-1}/(H^+)_t$
HNO ₃									
0.2741	0.2741	0.922	11.8	33.7	0.161	0.148	0.0127	0.539	0.046
.2490	.2490	.942	16.25	25.0	.0756	.0712	.0044	.286	.0175
HClO ₄									
2.00	.518	.909	9.97	35.0	.415	.377	.038	.728	.073
2.00	.519	.925	12.3	29.7	.282	.261	.021	.503	.040
2.00	.520	.937	14.9	25.0	.205	.192	.0129	.369	.0248
1.00	.508	.888	7.95	44.9	.845	.750	.095	1.48	.187
1.00	.509	.905	9.5	35.0	.350	.316	.033	0.622	.065
1.00	.511	.924	12.2	29.7	.240	.222	.018	.435	.035
1.00	.512	.938	15.1	25.0	.1665	.156	.010	.306	.020

TABLE VI
THERMAL CONSTANTS FOR THE HYDRATION OF MESITYL OXIDE AND DEHYDRATION OF DIACETONE ALCOHOL

Acid	μ , N	(H ⁺) N	Q_1 , kcal.	Q_{-1} , kcal.	ΔH of hydration, kcal.
HClO ₄	2.00	0.52	12.4	19.6	-7.2
HClO ₄	1.00	.51	12.9	21.3	-8.4
HNO ₃	0.25	.25	13.2	20.2	-7.0
Average			12.8 ± 0.15	20.4 ± 0.3	-7.5 ± 0.3

dehydration, 20.4 ± 0.3 kcal. Each value really is an average of the two heats of activation, one of the complexed, and the other of the uncomplexed, compound.

The heats of hydration at different ionic strengths are calculated as the difference in the heats of activation of the forward and reverse reactions (Table VI). The average value is 7.5 ± 0.3 kcal. Since the basicities of mesityl oxide and diacetone alcohol are comparable to that of water (Table III) and the heat of formation of the mesityl oxide oxonium complex from hydronium ion and the uncomplexed form has been shown to be essentially zero,³ the difference in the heats of oxonium formation of the two oxonium compounds is essentially zero. Thus the heat of hydration of the oxonium complex of mesityl oxide is the same as that of the uncomplexed form.

Experimental

The materials used and the method of analysis have been discussed previously.³ The rate experiments were started by adding mesityl oxide solution to an acid solution of the proper concentration and temperature. Samples were removed from time to time and analyzed.

Summary

Both mesityl oxide and its oxonium salt hydrate in dilute aqueous acid solutions at 25°. Di-

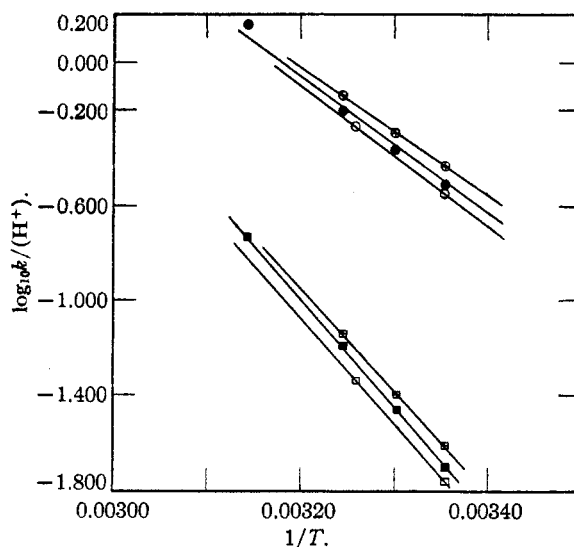


Fig. 4.—Plots of $\log_{10} k_1/(H^+)$ and $\log_{10} k_{-1}/(H^+)$ against $1/T$ for the hydration of mesityl oxide and the dehydration of diacetone alcohol.

Acid	N	μ	Hydration	Dehydration
HNO ₃	0.25	0.25	○	□
HClO ₄	0.5	1.0	⊕	⊕
HClO ₄	0.5	2.0	●	■

acetone alcohol and its oxonium salt dehydrate under the same conditions. Each reaction is first order with respect to the organic reactant and with respect to the hydronium ion concentration. In the hydration reaction, the mesityl oxide oxonium salt accounts for 34% of the total hydration in 2N perchloric acid. In the dehydration reaction, the diacetone alcohol oxonium salt accounts for 30% of the total dehydration in 2 N perchloric acid.

The oxonium complex constant $K_{D.A.}/(H_2O)$ for diacetone alcohol, where the hydrogen ion probably is coordinated at the carbonyl oxygen, was determined by the shift in the equilibrium

constant between diacetone alcohol and mesityl oxide with changing hydronium ion concentration. The value was found to be 0.3 at 25°.

The heat of hydration of mesityl oxide is $7.5 \pm$

0.3 kcal. The heat of activation is 12.8 ± 0.15 kcal. for the hydration of mesityl oxide and 20.4 ± 0.3 kcal. for the dehydration of diacetone alcohol.

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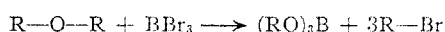
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Cleavage of Ethers with Boron Bromide. I. Some Common Ethers

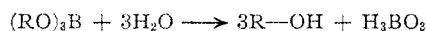
BY F. L. BENTON AND T. E. DILLON

Ether cleavage has been effected by the action of acid halides and anhydrides on ethers in the presence of metallic halides¹ as catalysts. Aluminum bromide² and boron chloride,³ however, have been shown to cleave ethers even in the absence of acid halides and anhydrides. In each case it has been established^{2,3,4} that the reaction takes place in the following steps: first the formation of a complex between the ether and metallic halide, and second the disproportionation of the complex resulting in cleavage of the ether.

The marked ability of boron halides to form complexes with ethers, and the ease with which etherates of boron chloride disproportionate led to the assumption that boron bromide might prove a very suitable reagent for cleaving ethers. In all cases boron bromide and the ether were allowed to react in a proportion of one mole of boron bromide to three moles of ether. Under those conditions our results indicate that the reaction proceeded according to the equation



Hydrolysis of the orthoboric ester may be expressed by the equation



Ethers chosen for cleavage included simple alkyl ethers in which the alkyl groups were primary or secondary, and alkyl phenyl ethers in which the alkyl group was primary or secondary while in certain cases the phenyl group was substituted. Cleavage of simple alkyl ethers yielded an alcohol and alkyl bromide, while the alkyl

phenyl ethers consistently yielded phenols corresponding to the phenyl group and alkyl bromides. The phenyl group, therefore, directs the course of the disproportionation of the boron bromide ether complex. The same effect was observed in the case of benzyl *n*-propyl ether, which yielded benzyl bromide and *n*-propyl alcohol instead of a mixture of products. The presence of substituent groups on the phenyl portion of the ether did not seem to affect the course of the cleavage, nor did any undesirable effects result when the reaction was carried out in an inert solvent. No disproportionation of the cleavage products or rearranged fragments was observed. That the method is applicable to the cleavage of sterically hindered methoxyls is indicated by the fact that mesityl methyl ether was cleaved with out difficulty.

TABLE I
CLEAVAGE REACTIONS WITH BORON BROMIDE

Ether	R-OH	Products	
		Yield, %	R-Br
Diethyl	Et	61	Et
Diisopropyl	<i>i</i> -Pr	50	<i>i</i> -Pr
Di- <i>n</i> -butyl	<i>n</i> -Bu	62	<i>n</i> -Bu
Isopropyl phenyl	Ph	64	<i>i</i> -Pr
<i>n</i> -Butyl phenyl	Ph	75	<i>n</i> -Bu
2-Bromophenyl methyl	2-Br-Ph	81	
Mesityl methyl	Mesitol	87	
Benzyl- <i>n</i> -propyl	<i>n</i> -Pr	71	Ph-Me

Experimental

Reagents.—Boron bromide was prepared by the action of boron fluoride on anhydrous aluminum bromide according to the method of Gamble.⁵ Diethyl, diisopropyl, di-*n*-butyl phenyl, and *o*-bromophenyl methyl ethers were products of the Eastman Kodak Co. Mesityl methyl ether was kindly furnished by Dr. G. F. Hennion, while isopropyl and benzyl *n*-propyl ethers were prepared by the Williamson synthesis.⁶ With the exception of *o*-bromophenyl methyl ether all ethers were purified for use by

(1) H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932); H. W. Underwood, Jr., and G. C. Toone, *THIS JOURNAL*, **52**, 391 (1930); G. F. Hennion, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 2857 (1933); W. J. Monacelli and G. F. Hennion, *ibid.*, **63**, 1722 (1941); Ya. L. Goldfarb and L. M. Smorgonski, *J. Gen. Chem.* (U. S. S. R.), **8**, 156 (1938).

(2) P. Pfeiffer and E. Haack, *Ann.*, **460**, 156 (1928); P. Pfeiffer and W. Loewe, *J. prakt. Chem.*, **147**, 293 (1937).

(3) E. Wiberg and W. Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 22 (1931).

(4) E. Wiberg and W. Sütterlin, *ibid.*, **202**, 37 (1931).

(5) E. L. Gamble, P. Gilmont and F. J. Stiff, *THIS JOURNAL*, **62**, 1257 (1940).

(6) R. A. Smith, *ibid.*, **55**, 3718 (1933).