witch–Wood effect for pairs of methyl radicals would entail also decreased methane production resultant from action of free methyl on substrate molecules. Table II shows such an expected drop in $G(CH_4)$ in going from electron to pile bombardment. However, except in the case of *t*-butylbenzene where $G(C_2)$ represents largely yield of ethane, we must be cautious in assuming a significant relationship between increase of $G(C_2)$ and decrease of $G(CH_4)$. There is the possibility that increase of $G(C_2)$ reflects increased ring rupture.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates and Temperature Coefficients in the Hydration of Gaseous Isobutene by Dilute Aqueous Nitric Acid[1]

BY JOSEPH B. LEVY, ROBERT W. TAFT, JR., DAVID AARON AND LOUIS P. HAMMETT

We have developed a method for measuring the rate of reaction of a gaseous olefin with an aqueous acid solution from which the rate of reaction of the olefin at unit fugacity may be determined with a probable error of 1% or less, and have applied it to the reaction of isobutene with approximately 0.1 and 1 *m* nitric acid. The energies of activation derived from measurements over a 20° range have a probable error of 0.13 kcal. Because of uncertainties about the distribution constant of olefin between solution and gas phase these rates cannot be directly compared with previous measurements of the rate at unit concentration of dissolved olefin. The rate of reaction at unit fugacity shows an even stronger medium effect than the rate at unit concentration, showing that the effect depends primarily on a sharp variation with acid or salt concentration of the ratio of the activity coefficient of OH_3^+ to the activity coefficient of the likewise positively charged transition state.

A major weakness in present thinking about the problem of structure and reactivity in organic compounds arises from uncertainty about the extent to which the relative reactivity of two substances is determined by other factors than the energy of activation. This is equivalent to uncertainty about the extent to which observed relative reactivities are determined by the accident of the temperature at which measurements are made. The difficulty lies not merely in lack of sufficient data but also in doubts about the validity of existing data which derive from the inherent difficulty of determining energies of activation with sufficient precision. Thus Lucas and co-workers[2] in a valuable study of the acid catalysis of the hydration of olefins to alcohols report without comment data which indicate that in dilute nitric acid isobutene reacts 1.72 times more rapidly than trimethylethylene but that the energy of activation is 4.5 kcal. greater for the more reactive olefin. If these figures are correct the order of reactivity must reverse between 25 and 0° with isobutene less reactive than trimethylethylene at the lower temperature. But the figure of 4.5 kcal. is computed from measurements of four rate constants, one for each of the olefins at each of two temperatures which differ by ten degrees, and a randomly distributed error of only 5% in each of these rate constants would lead to a probable error of 1.8 kcal. in the energy of activation. While it is hardly probable that the energy of activation of isobutene is 0.3 kcal. less than that of trimethylethylene, as must be the case if no reversal of the order of reactivity is to occur at any temperature, it is by no means certain that it is as much as 4.5 kcal. greater. Clearly the temperature coefficients of the hydration reactions of olefins deserve further attention, and we have sought a method of measuring the rate which should be of the highest possible precision. After considering and discarding those used by previous investigators[2,3] we have come to one whose application to isobutene is the subject of the present article.

Principle of the Method.—The method depends upon the drop in the vapor pressure of the volatile olefin from the aqueous solution which accompanies the progress of the reaction. The apparatus was modified from one used by Greenspan, LaMer and Liotta[4] for measuring the rate of evolution of a gas in a constant volume system. We use the symbols

v_l = volume of acid solution
v_g = volume of gas phase
r = v_g/v_l
p = observed pressure at time t
p_s = partial pressure of the solvent
P = $p - p_s$ partial pressure of gaseous olefin at time t
P^0 = partial pressure of olefin at time 0
P^e = partial pressure of olefin when reaction has reached equilibrium
C_a = concentration of alcohol in solution at time t
C_a^e = concentration of alcohol in solution at equilibrium
C_0 = concentration of olefin in solution at time t
C_0^0 = concentration of olefin in solution at time 0
h = C_0/P the distribution constant of olefin between liquid and gas phases
k_c = rate of conversion of olefin to alcohol in solution at unit concentration of olefin in solution
k_p = rate of conversion of olefin to alcohol in solution at unit pressure of olefin in gas phase; $k_p = k_c h$
k_{-1} = rate of conversion of alcohol to olefin in solution at unit concentration of alcohol in solution
s = $-\mathrm{d}\ln(P - P^e)/\mathrm{d}t$

For this reversible reaction we have, provided equilibrium is at all times maintained in the distribution of olefin between gas and liquid, the basic rate equation

$$\frac{\mathrm{d}C_a}{\mathrm{d}t} = k_c C_0 - k_{-1}C_a = k_p P - k_{-1}C_a \qquad (1)$$

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (a) H. J. Lucas and W. F. Eberz, THIS JOURNAL, **56**, 460 (1934); (b) H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934); (c) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

[3] F. G. Ciapetta and M. Kilpatrick, THIS JOURNAL, **70**, 639 (1948).

[4] J. Greenspan, V. K. LaMer and S. Liotta, *ibid.*, **59**, 1606 (1937).

From material balance considerations

$$C_a = \frac{1}{v_1}\left[\frac{v_g}{RT}(P^0 - P) + v_1(C_a^0 - C_0)\right]$$
$$= \left(\frac{r}{RT} + h\right)(P^0 - P) \qquad (2)$$

Differentiating Eq. (2) with respect to time and combining with Eq. (1) we get

$$-\left(\frac{r}{RT} + h\right)\frac{dP}{dt} = k_pP - k_{-1}C_a \qquad (3)$$

At equilibrium $dP/dt = 0$ hence

$$0 = k_pP^e - k_{-1}C_a^e \qquad (4)$$

By eliminating P^0 and $C_a - C^a$ between Eq. (2), (3) and (4) we can get

$$s = -\frac{1}{P - P^e}\cdot\frac{dP}{dt} = \frac{k_p}{h + r/RT} + k_{-1} \qquad (5)$$

It follows from Eq. (5) that a plot of log $(P - P^e)$ against time should be a straight line in any given experiment. This prediction is abundantly confirmed in all our work. No systematic curvature has been observed in any such plot, and, as the low values of the probable error of s listed in Table I demonstrate, the scatter of the experimental points is small.

From Eq. (2), (4) and (5) we get

$$k_{-1} = \frac{P^e}{P^0}s \qquad (6)$$

Since P^0 may be determined with moderate precision by methods described in the experimental part, and P^e and s may be determined with excellent precision, k_{-1} may be computed with a precision which is adequate in all the cases we have investigated. With k_{-1} known, values of k_p and h may be derived from a series of measurements of this slope s at varying values of the volume ratio r.

Equation (5) may be put in a number of forms from which the desired coefficients may be derived from the slope and intercept of a linear plot of known quantities. We have used the equation

$$\frac{RT}{r(s - k_{-1})} = \frac{1}{k_p} - \frac{h}{k_p}\frac{RT}{r} \qquad (7)$$

and have plotted $RT/r(s - k_{-1})$ against RT/r. This choice of methods of obtaining values of k_p and h was dictated by the following considerations. As the typical data of Table I show the absolute probable error in s is greater the larger the value of s and the per cent. probable error is nearly constant. These probable errors are calculated from the scatter in the plots of Eq. (5). The uncertainty in r is unimportant compared with that in s. Consequently the application of simple least squares methods to the likewise linear plot of, for instance, $1/(s - k_{-1})$ against r would give improper weighting, since the method assumes that the absolute probable error is the same for all points. The nature of our system is however such that the product $r(s - k_{-1})$ is nearly constant, and a constant relative probable error in s leads to a nearly constant absolute probable error in the value of the ordinate in the plot of Eq. (7), and therefore to a proper weighting in the least square procedures.

TABLE I

HYDRATION OF ISOBUTENE AT 14.96° IN 0.973 m HNO_3

RATE OF PRESSURE FALL

$10^3 r/RT$	$10^3 s_{obsd.}$	Probable error of $10^3 s$ Absolute	%	$10^3 s_{calcd.}$	Difference, %
34.9	1.861	4.09	0.22	1.863	0.1
43.3	1.548	2.53	.16	1.554	.4
54.0	1.280	2.00	.16	1.283	.2
63.6	1.145	1.93	.17	1.110	3.2
73.4	0.960	1.31	.14	0.975	1.5
84.8	.845	1.15	.14	.855	1.2
100.1	.744	0.90	.12	.733	1.5
114.2	.640	.90	.14	.648	1.2
		Aver.	0.16	Aver.	1.2

The column headed $s_{calcd.}$ in Table I contains values of s calculated from Eq. (7) using values of the constants k_p and h obtained in this way from the observed values of r and s. The excellent agreement between observed and calculated values obtained in this typical case illustrates the validity of Eq. (5) and (7).

In our experiments on the hydration of isobutene k_{-1} was negligible compared with s (less than 1%) at 35° and lower temperatures and amounted to a small correction term at 45° and 55°.

While the estimated uncertainty in the values of the quantity k_p obtained in this way is satisfactory, the method is not a suitable one for the estimation of the distribution constant h, because the near constancy of the left-hand side of Eq. (7) permits no precise determination of the slope h/k_p. The only possible solution of this problem, that of using a wider range of values of the variable RT/r is precluded by the necessity of maintaining very active agitation of our two-phase system in order to ensure distribution equilibrium between gas and liquid.

Since we have been unable to find any other method of sufficient precision for determining the distribution coefficient of olefin between the gas phase and the acid solution in which it reacts rapidly, our method does not supply a means of determining the ordinary rate constant k_c to better than a rough approximation. From the point of view of general theory the rate constant k_p is however a quantity of inherent interest. In view of the low pressures (< 30 cm.) of gas involved, k_p may be taken to represent to a good precision the rate of reaction of the olefin at unit fugacity, whereas k_c is the rate at unit concentration in solution. In terms of the absolute rate theory k_p is equal to kT/h times the equilibrium constant for the formation of the activated state in the hydration reaction in solution from gaseous olefin, whereas k_c bears the same relation to the equilibrium constant for the formation of the activated state from the dissolved olefin.

Experimental

Apparatus.—The apparatus used is shown in Fig. 1. The flexible glass spiral I permits the 40-ml. reaction flask F containing the acid to be vigorously shaken with an amplitude up to 2 cm. The indented neck of F acts as a baffle which prevents liquid from entering the spiral. The 30-cm. graduated manometer, M, was of 1 mm. inside diameter, and was readable to ±0.01 cm. The diameter of R was twenty to thirty times as great as M so that changes of the mercury level in R during an experiment were negligible. R' was of about 4-ml. capacity and was sealed off under a pressure of about 0.2 mm. S and T are precision stopcocks. Between S, I and R all tubing was of 1 mm. inside diameter. The vigorous shaking of the reaction flask by the offset shaking device[4] gave rise to oscillation of the entire apparatus preventing any serious clinging of the mercury in the manometers.

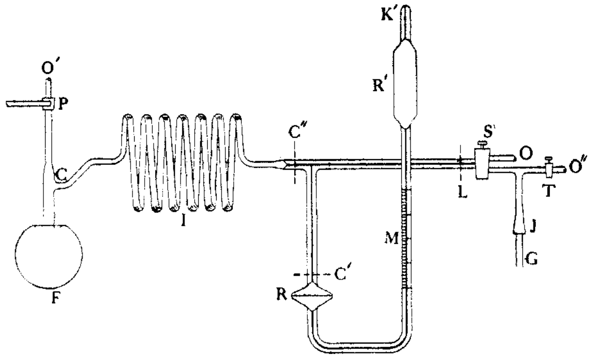

Fig. 1.

Procedure.—Two different experimental procedures were used in obtaining the results reported. In Procedure A a known volume of nitric acid was introduced into F *via* a small funnel extending through the length of P. O′ was then sealed off and most of the air removed from the system through O. Stopcock S was then closed. The tube C containing a few ml. of liquid olefin was then attached to the apparatus by a ground joint at J, the olefin was frozen by surrounding the tube by a Dry Ice–trichloroethylene-bath and the tube was evacuated by an oil-pump *via* O″. T was then closed, C warmed to room temperature, S opened to let in enough gaseous olefin to register a suitable pressure on M. With S closed the contents of F were frozen with the Dry Ice-bath. The system was pumped down *via* S and O to a pressure of about 1 mm., and the apparatus sealed off in the neighborhood of L. Apparatuses, mounted in pairs on a stand, were placed in a thermostat, and the flasks set to shake. When temperature equilibrium was attained, manometer readings were taken at regular time intervals until a sufficient number of readings were obtained. Shaking was continued until there was no further pressure drop (approximately ten half-lives). This was the value taken as the infinity reading. In Procedure B all of the apparatus to the right of S was omitted. The nitric acid was introduced from a Bureau of Standards calibrated buret into F as in Procedure A. O was sealed off, S closed, and the nitric acid solution frozen by immersing F in a Dry Ice–CCl_4–$CHCl_3$-bath. S was then opened to a Hyvac pump and the system evacuated to 0.1 mm. or less. S was closed and the nitric acid solution in F melted, shaken gently to remove bubbles, and refrozen. The system was again evacuated to less than 0.1 mm. This procedure was repeated until the solution had been melted and refrozen three times. The purpose of this operation was to remove dissolved air from the system which is mechanically trapped by the ice particularly on the first freezing. An airtight train from the isobutene storage cylinder was then connected at O *via* precision g.s. joints, and this system evacuated to less than 0.1 mm. With the nitric acid in F at room temperature, isobutene was introduced directly from its cylinder, a needle valve being used to regulate the desired olefin pressure approximately 20 cm. The system was then frozen by immersing F in a liquid nitrogen-bath, evacuated to 0.5 mm. pressure, and sealed off at L. When it was unnecessary to take account of reversibility the reaction systems were brought to reaction temperature in the thermostat, and readings of pressure and time were made as in Procedure A. In those cases in which the reversibility was significant, the frozen system was brought to near reaction temperature without shaking, and the value of $P°$ needed in Eq. (9) was obtained by extrapolation of a plot of log P to zero time, which was taken as the time when shaking was started. It was therefore assumed that no reaction occurred during the warming up period in the absence of shaking.

The principal difference between these two techniques is that by A experiments are made under a partial pressure of 1 to 2 cm. of air, while B essentially all air is removed. Since, as appears to be the case, air does not react in this system and has no catalytic effect, the difference between the two procedures is unimportant when the hydration is essentially irreversible. The determination of $P°$ requires the use of Procedure B for significantly reversible reactions.

The rate constants, $10^5 k_p$, determined by Procedure A for isobutene in 0.973 *m* acid were: 15.00° – 7.81 ± 0.04; 25.00° – 20.8 ± 0.18; 35.00° – 55.9 ± 1.0. At 15 and 35° these are in good agreement with those obtained by Procedure B, which are listed in Table IV; we attribute the disagreement in the results at 25° to the fact that the results obtained by Procedure B were obtained after much greater experience with apparatus and techniques, by an improved method, and over a greater range of r values. We have therefore rejected the values obtained by method A in this case.

Temperatures were controlled to ±0.02° and were measured by a thermometer calibrated by the National Bureau of Standards. Times were read to ±0.05 min.

The isobutene was Phillips Petroleum Company research grade (99.44 mole per cent.).

The Volume Determination.—The quantity v_l is known from the volume of nitric acid solution used. v_g was determined from the value of v_l and a measurement of the total volume of the apparatus, the latter being determined in 3 sections which were then sealed together at C′ and C″ (Fig. 1).

The volume of the section containing the flask and spiral was found by weighing it empty and then full of water. With O′ sealed off this section was evacuated and then allowed to fill with distilled water from a reservoir by way of the third arm of a three-way stopcock. The height of the water column in P was measured from a reference point C. Duplicate measurements agreed to ±0.01 ml.

The volume of the T tube section was measured similarly using mercury instead of water. The volume of the last section was determined under the conditions of an experiment, *i.e.*, with the mercury in the manometer in the intermediate reading range and with the cross section in R a maximum. This whole section was filled with mercury and enough of the mercury withdrawn at C′ under reduced pressure to give the former condition. Then enough mercury was withdrawn through a capillary into a weighed flask to fulfil the second condition. From the weight of this mercury the gas volume of this section was found with an accuracy of 0.01 ml.

The points C′ and C″ where the sections were sealed together and the point L where the apparatus was sealed off after filling all fall in regions of the 1 mm. capillary tubing. Since the volume of such tubing per cm. of length is 0.008 ml., it is possible to make these seals with an uncertainty in volume not exceeding 0.01 ml. When the apparatus was sealed at O′ just prior to carrying out an experiment, the volume of tubing in P from O′ to the calibration point was accounted for from the length of this section and the volume per unit length of the tubing (0.12 ml. per cm.). The total of the above corrections rarely exceeded 0.4 ml., so that errors in volume so introduced could not reasonably exceed ±0.05 ml. for the entire apparatus.

Strictly speaking v_g is not constant during an experiment, but decreases by an amount equal to the change in pressure multiplied by the volume per cm. of tube M (0.008 ml.). This volume change amounted in no case to as much as 1% and introduced therefore no error of significance.

Effect of Shaking Rate on Equilibrium of between Gas Phase and Solution.—The validity of Eq. (5) and (7) is in itself strong evidence that the requirement of distribution equilibrium between gas and liquid is maintained. We have further carried out extensive experiments on the effect of variations in shaking rate as measured by the frequency of oscillation of the flask. Some of the pertinent data are presented in Table II.

Table II

The Effect of Shaking Rate on the Rate of Pressure Drop

Isobutene at 35°, 0.973 *m* nitric acid

$10^3 r/RT$ l.$^{-1}$ atm.$^{-1}$	$10^3 s/2.303$ at the various shaking rates 180 r.p.m.	280 r.p.m.	320 r.p.m.	360 r.p.m.
39.3	4.23	5.52	5.41	
54.7		4.17	4.24	
80.2	1.73	2.87	2.87	
99.3		2.25		2.27
139.9	1.23	1.70		1.69
120.5	1.45	2.08	2.02	2.02

It is apparent that the rate of pressure drop does not increase above a shaking rate of 280 r.p.m., lending further support to the conclusion that saturation equilibrium is maintained at the shaking rate of 350 r.p.m., which was used in our experiments.

Results and Discussion

Measurements of the rate of hydration of isobutene were made with 0.973 and 0.0909 *m* nitric acid, data being obtained at three temperatures with each acid concentration. The results are given in Table III. The probable errors listed were computed by standard methods from the scatter of the points in the plot of Eq. (7).

TABLE III

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS ISOBUTENE BY AQUEOUS NITRIC ACID IN 10^5 MOLE-L.$^{-1}$ ATM.$^{-1}$-MIN.$^{-1}$

Nitric acid concentration 0.973 mole/l.

Temp., °C.	14.96	24.89	34.84
k_p	7.88	21.9	55.5
Probable error	0.09	0.14	0.40

Nitric acid concentration 0.0909 mole/l.

Temp., °C.	34.93	44.90	54.94
k_p	3.02	7.54	17.95
Probable error	0.02	0.05	0.18

The values of 10^5 k_{-1} which we have found are 2.0 at 45° and 10 at 55°. The quantity is too small for measurement at 35° and lower.

Our data lead through Eq. (7) to values of the distribution constant *h* which, as we have pointed out, cannot be expected to have more than order of magnitude precision. The values obtained are in 10^3 mole-l.$^{-1}$-atm.$^{-1}$: for the 0.973 molar acid 7.4 at 15°, 5.7 at 25°, 2.6 at 35°; for the 0.0909 molar acid 5.3 at 35°, 2.4 at 45°, 5.4 at 55°. Since *h* is equal to the ratio k_p/k_c, we may calculate values of *h* from the Lucas and Ebertz values of k_c and our values of k_p where these have been measured at the same temperature and approximately the same acid concentration. On this basis we get a value of 6.6 $\times$ 10^{-3} for 0.973 *m* acid at 25°, which is 16% greater than the value from Eq. (7), and 3.92 $\times$ 10^{-3} for 0.0909 *m* acid at 35° which is 26% less than the value from Eq. (7).

Plots of log k_p against $1/T$ are linear within the precision of measurement. Thus the value of 10^5 k_p in 0.973 molar acid at 24.89° computed on the basis of this linearity from the values at the higher and lower temperatures is 21.6 ± 0.30, compared with the observed value of 21.9 ± 0.14. In 0.0909 molar acid the value computed for 44.90° by this interpolation is 7.55 ± 0.09, the observed value is 7.54 ± 0.05. This being so, the best value of the energy of activation $\Delta H^{\ddagger}$ is obtained from the slope of this plot as defined by the points for the extreme temperatures, *i.e.*, from the equation

$$\Delta H^{\ddagger} = -\frac{R \ln k_2/k_1}{1/T_2 - 1/T_1} - RT \qquad (8)$$

where T_2 and T_1 are the highest and lowest temperatures of the range, and T is a mean temperature.

The values of $\Delta H^{\ddagger}$ thus obtained are 16.71 ± 0.13 kcal. for 0.973 *m* acid and 17.27 ± 0.12 kcal. for 0.0909 *m* acid. These values represent the difference in enthalpy between the activated state in solution on the one hand and the *gaseous* olefin and aqueous acid on the other. The $\Delta H^{\ddagger}$ value of 23.19 kcal. derived from the temperature coefficient of the k_c values in 0.1005 *m* nitric acid of Lucas and Eberz[2a] represents a similar difference except that the olefin is dissolved, and the 5.9 kcal. difference between the two $\Delta H^{\ddagger}$ values for the dilute acid should therefore equal the heat of vaporization of isobutene from dilute aqueous solution. This is almost certainly larger than the heat of vaporization of isobutene from water solution, since the heat of vaporization of pure liquid isobutene is only 4.92 kcal.[5] and solutions of hydrocarbon and water doubtless show a positive deviation from ideality. We cannot speak with the same confidence about the heat of vaporization from acid solution since the comparison of our results with those of Lucas and Eberz indicates that the activity coefficient of dissolved olefin decreases with increasing acid concentration.

Entropies of activation, calculated from the formula

$$\Delta S^{\ddagger} = \frac{RT \ln k_2 - RT_1 \ln k_1}{T_2 - T_1} - R \ln \frac{kT}{h} - R \qquad (9)$$

where T_2 and T_1 are again the extreme temperatures, are found to be −27.3 ± 0.4 cal./deg. in 0.973 molar acid and −31.2 ± 0.4 in 0.0909 *m* acid. The difference 3.9 ± 0.6 is not reliably distinguishable from the 4.72 cal./deg. computed on the ideal dilution law from the change in the concentration of the catalyzing hydrogen ion.

One of the important results of Lucas's investigations of the hydration rates of olefins is that medium effects are surprisingly large. This phenomenon has also interested other investigators.[3,6] For instance, Lucas and Ebertz found isobutene to react 15.31 times faster in 1 *m* nitric acid than in 0.1005 *m* acid at 25°. This ratio is 54% larger than the ratio of the acid concentrations. In terms of the Brønsted relation

$$k_c = k_c^0 \, [\mathrm{OH_3^+}] \, \frac{\gamma_{\mathrm{H^+}}\gamma_0}{\gamma_{\ddagger}} \qquad (10)$$

where γ_0 is activity coefficient of olefin, $\gamma_{\mathrm{H^+}}$ that of $\mathrm{OH_3^+}$ and $\gamma_{\ddagger}$ that of the transition state this means that the ratio $\gamma_{\mathrm{H^+}}\gamma_0/\gamma_{\ddagger}$ increases sharply with increasing acid concentration. Our values of k_p show an even larger medium effect, the ratio of the rates in 0.973 and 0.0909 *m* acid at 35° being 18.38, which is 72% greater than the ratio of the acid concentrations. The applicable equation here is

$$k_p = k_p^0 \, [\mathrm{OH_3^+}] \, \frac{\gamma_{\mathrm{H^+}}}{\gamma_{\ddagger}} \qquad (11)$$

if, as is probable at the low pressures involved, the fugacity of the gaseous olefin may be taken equal to its pressure. It follows that the large medium effect is primarily the result of a large effect of changing acid concentration on the ratio of the activity coefficients of $\mathrm{OH_3^+}$ ion and of the likewise positively charged transition state. The effect of the acid concentration on the activity coefficient of the

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(5) Selected Values of the Properties of Hydrocarbons, Circular of the National Bureau of Standards C461, p. 139.

(6) G. R. Lucas and L. P. Hammett, THIS JOURNAL, 64, 1938 (1942).

dissolved olefin is considerably smaller, and operates in a direction opposite to that produced by the changes in the activity coefficients of the ionic substances. There is a considerable presumption that the medium effect arises predominantly from a change with acid concentration of the energy of activation since the observed energy is 0.56 ± 0.18 kcal. lower for the 0.973 *m* acid than for the 0.0909 *m* acid.

A single experiment was made at 45° on the rate of pressure drop in a system composed of gaseous isobutene and a solution containing 0.0909 *m* nitric acid and 0.88 *m* potassium nitrate, at a value of the volume ratio *r* where an approximate estimation of the value of *h* sufficed to yield a value of k_p which should not be in error by more than 5%. The ratio of this value of k_p to that in 0.0909 *m* acid without the salt was 1.37. This implies that the effect of added potassium nitrate on the quantity $\gamma_{H^+}/\gamma_\pm$ is materially smaller than the effect of the same amount of additional nitric acid. The close equivalence of the effects of added acid and salt on the values of $k_c/[\mathrm{OH}_3^+]$ which Lucas and Ebertz observed must depend therefore upon a compensation in which the different effects of acid and salt on $\gamma_{H^+}/\gamma_\pm$ are cancelled by different effects of acid and salt on γ_0.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PHOSPHATE DIVISION, MONSANTO CHEMICAL COMPANY]

The Vapor Phase Reaction between Phosgene and Alcohols

BY J. H. SAUNDERS, R. J. SLOCOMBE AND EDGAR E. HARDY

The vapor-phase reaction between phosgene and alcohols has been demonstrated. With an excess of phosgene, the principal products from primary and secondary alcohols were the corresponding chloroformates. In one experiment with an excess of *n*-propyl alcohol, the carbonate was obtained in good yield. *t*-Amyl alcohol was converted principally to *t*-amyl chloride. Small amounts of alkyl chloride and olefin were formed in a number of the experiments.

Although the liquid-phase reactions of phosgene have been widely investigated, the reactions of that compound in the vapor-phase are relatively unexplored. The gas-phase preparation of isocyanates and carbamyl chlorides in high yields from amines[1] suggested similar reactions with other active hydrogen compounds, such as alcohols, which are reported here.

It is well known that alkyl chloroformates decompose in the gas phase to give the corresponding olefin, alkyl chloride, carbon dioxide and hydrogen chloride.[2] For example, the half-life of isobutyl chloroformate has been reported to be one hundred and sixty minutes at 267°, sixteen at 302°.[3] Furthermore, it is considered possible that phosgene and an alcohol could react in such a way as to give directly an olefin and an alkyl chloride, without the intermediate formation of a chloroformate. Consequently the products expected from this study included all of the above mentioned compounds. The reaction was investigated primarily with the object of preparing substituted chloroformates, however.

By using sojourn times of the order of three seconds and temperatures of 100–250°, 50–80% yields of chloroformates were obtained from primary alcohols, methyl through octyl. A 69% yield of propyl carbonate also was realized. Isopropyl and cyclohexyl alcohols gave 55 and 73% of the chloroformates, respectively. *t*-Amyl alcohol, however, did not react completely, and was converted to the chloroformate in only 7% yield, isolated as the urethan. Cyclohexyl and octyl chloroformates were also converted to the urethans. Phenol was recovered unchanged, even when temperatures as high as 430° were used. It is possible that the phenol would have reacted at much longer sojourn times, however.

In many of the experiments small amounts of olefin and alkyl chloride were obtained. The data did not show conclusively that these products were formed in the vapor-phase; they may have been the result of decomposition during standing or distillation.

It was demonstrated conclusively that the reaction between methanol and phosgene at 85–100° took place in the vapor-phase reactor. Treatment of the crude product with phenyl isocyanate gave no methyl carbanilate, showing the absence of unreacted methanol in the crude chloroformate. The yield of chloroformate was 73%. On the other hand, methanol saturated with phosgene at 10–15° and treated with phenyl isocyanate as before gave 61% of methyl carbanilate and only 13% of the chloroformate.

Experimental

General Method.—The apparatus and procedure were essentially the same as those described for the vapor-phase reaction between amines and phosgene,[1] with the following modifications. The thermowell in the reactor extended to within 1 in. of the tip of the phosgene inlet tube so that the temperature could be measured at any point in the reaction zone. An iron–constantan thermocouple was used for this measurement. The reaction zone had a volume of 95 cc., and feed rates were such that sojourn times of 3–4 sec. were obtained. The phosgene:alcohol molar ratio was 1.1–2.0 in all cases except in the preparation of propyl carbonate. The receiver was cooled in an ice-water-bath. The best yields and corresponding temperatures are shown in Table I.

The temperatures listed are those observed at the point of mixing of phosgene and alcohol. The temperature farther up the reactor was generally 10–20° higher. All yields are based on the alcohol. All additional information is given in Table II or under the heading of the alcohol used.

Preparation of Urethans.—To obtain a check on the yields achieved by distillation (Table I), certain of the above experiments were repeated and the crude product was converted to the urethan, as follows. An equal volume of isohexane was added to the crude condensate. Concentrated aqueous ammonia (sp. gr. 0.90) was added with stirring, at

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(1) R. J. Slocombe, E. E. Hardy, J. H. Saunders and R. L. Jenkins, THIS JOURNAL, **72**, 1888 (1950).

(2) A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948).

(3) L. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).