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Enthalpies and Entropies of Activation for the Hydration of Dissolved Isobutene and Trimethylethylene from the Thermodynamic Properties for Solution of Gaseous Olefins in Aqueous Nitric Acid[1,2]

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A very careful investigation of the rate of hydration, k_p, of gaseous isobutene and trimethylethylene at unit pressure by one molar nitric acid over a thirty to forty degree temperature interval shows the enthalpies of activation for the gaseous reactants to be (within the precision of measurement) independent of temperature. On the other hand, the rates of hydration, k_c, of these dissolved olefins at unit concentration for the same temperature ranges lead to enthalpies of activation for dissolved reactants which are quite temperature dependent. The latter thermodynamic properties have been obtained from the former using enthalpies of solution of the gaseous olefins obtained from measured temperature coefficients of the distribution constants. The relative enthalpy of activation of dissolved trimethylethylene (using isobutene as standard of comparison) is found to be $+1.1 \pm 0.3$ kcal./mole in contrast to the value of -4.4 kcal./mole reported earlier by Lucas, *et al.* The dangers of deriving relative enthalpies of activation from relative rate constants only ten degrees apart are emphasized.

Enthalpies of activation for the hydration of gaseous trimethylethylene and isobutene by one molar nitric acid have recently been reported by Hammett and co-workers which indicate a 1.5 ± 0.6 kcal./mole greater value for the latter olefin.[4] The rate of hydration of gaseous trimethylethylene at unit pressure, k_p, at 25° is 0.71 times that for isobutene. Earlier, Lucas and co-workers reported data indicating that the enthalpy of activation for the hydration of these dissolved olefins by one-tenth molar acid was 4.4 kcal./mole greater for isobutene.[5] The hydration rate of dissolved olefin at unit concentration, k_c, at 25° was given for trimethylethylene as 0.58 times that of isobutene.

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 aqueous acid solution from gaseous olefin, whereas k_c bears the same relation to the equilibrium constant for the formation of the activated state from dissolved olefin. Accordingly, the above two sets of data differ by the unknown thermodynamic properties associated with the distribution of the gaseous olefins between the vapor state and the aqueous acid solution.

In reporting their results, Hammett, *et al.*, pointed out that if the data of Lucas and co-workers are correct the order of reactivity (of dissolved olefins) must reverse between 25 and 0° with isobutene less reactive at the lower temperature. On the other hand if the enthalpy of activation for isobutene were about 0.3 kcal. less than that for trimethylethylene no reversal of order would occur at any temperature. It was pointed out that in addition to uncertainties in the method of measurement, the temperature coefficient results of Lucas, *et al.*, were to be suspected solely on the basis of the inherent experimental difficulty in determining precise enthalpies of activation, for rates had been obtained over only a 10° interval.

Several reasons suggest that the results of Hammett, *et al.*, and of Lucas, *et al.*, are inconsistent. In view of the 1.6 kcal. greater enthalpy of vaporization from the pure liquid state at 25° for trimethylethylene than isobutene,[6] it seems quite unlikely that the enthalpy of vaporization from aqueous acid solution would be 2.9 kcal. greater for the latter olefin. This is the required result for consistency between the two sets of data. Second, an extensive study of the effect of olefin structure on hydration free energies and enthalpies of activation for dissolved olefins has shown quite generally that structure affects both these quantities in the same direction.[7] The lower enthalpy of activation and lower reactivity reported by Lucas, *et al.*, for trimethylethylene is clearly inconsistent with this generalization. On the other hand, the results of Hammett, *et al.*, would be consistent with the generalization and the relative reactivities given by Lucas, *et al.*, if the enthalpy of vaporization from nitric acid solution were more than 1.5 kcal. greater for trimethylethylene than isobutene. Third, Lucas and Liu's results lead to an entropy of activation (at unit trimethylethylene and acid concentration) of -14 cal./deg., a value appreciably lower than that for any other aliphatic olefin which has been investigated.[8]

An accurate knowledge of the relative enthalpies of activation of these dissolved olefins is essential from the standpoint of theoretical considerations of the effect of structure on reactivity. Thus, if the effect of replacing a H atom in isobutene by a methyl group to give trimethylethylene is to introduce *only* direct hyperconjugation or inductive effects on the hydration rates, the relative enthalpy of activation of trimethylethylene must be about $+0.3$ kcal./mole (*i.e.*, $\Delta\Delta F^{\ddagger} = \Delta\Delta H^{\ddagger} = \Delta\Delta E_p{}^{\ddagger 8c}$).

Because of the importance of resolving the uncertainties discussed above, we have determined the distribution constants, h, for trimethylethylene and isobutene between the vapor state and the condensed phases, water and aqueous nitric acid solutions, over a relatively wide range of temperatures

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[1] Taken in part from the Ph.D. Thesis of E. Lee Purlee, The Pennsylvania State University, June, 1954.

[2] The work reported herein was carried out on Project NR055-295 between the Office of Naval Research and the Pennsylvania State University.

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[4] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); (b) *ibid.*, **75**, 3955 (1953).

[5] (a) H. J. Lucas and W. F. Everz, *ibid.*, **56**, 460 (1934); H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934).

[6] (a) "Selected Values of the Properties of Hydrocarbons," Circular of the National Bureau of Standards C461, p. 139; (b) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 2767 (1949).

[7] *Cf.*, for example, P. Riesz and R. W. Taft, Jr., *ibid.*, in publication.

[8] (a) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952); (b) *ibid.*, in press; (c) *cf. ibid.*, **75**, 4534 (1953), for symbolism.

(0–50°). We have also extended the measurement of the rates of hydration at unit pressure of these olefins by one molar nitric acid to cover temperature intervals of 40° for trimethylethylene (0–40°) and 30° for isobutene (15–45°). The results of these measurements confirm the suspected serious discrepancy in the data discussed above.

Experimental

Materials.—The trimethylethylene was a center cut (b.p. 38.46–38.51° (760 mm.), $n^{20}\text{D}$ 1.3875) from the fractionation of a sample of Phillips Petroleum Company research grade (99.59 mole %) product. The isobutene was Phillips research grade (99.44 mole %) product.

Determination of the Distribution Constants, *h*.—The procedure used has been described elsewhere.[9]

Measurement of Rate Constants, k_p.—For isobutene the procedure used was identical with that previously described—Procedure B, ref. 4a.

For trimethylethylene the following modification of procedure B was made. A 100-ml. reaction flask (F)—see Fig. 1 of ref. 4a—was used in place of the 50-ml. flask, permitting the attainment of lower r/RT values (r is the ratio of vapor volume to liquid in the apparatus). Tube (G), the liquid olefin container was sealed directly to the system, *i.e.*, the ground glass joint (J) was eliminated. A second precision one-way stopcock (T′) was introduced at (O). The nitric acid solution was introduced and degassed in (F) as described in the isobutene work. With (S) closed, the liquid olefin was similarly degassed by freezing with a liquid nitrogen bath and evacuating *via* (O″). Finally, with both the acid solution and olefin frozen, the entire system was evacuated *via* (S) and (O″). The system was then completely immersed in a thermostat at the temperature of the desired rate determination. When temperature equilibrium was established, (S) was opened and enough olefin was allowed to evaporate into the system to give a convenient pressure reading on M, the system being held rigid during this operation. The system was quickly removed from the thermostat, the contents of (F) frozen, and the system sealed off at (L). The procedure was otherwise the same as referred to above.

In all of this work plots of log $(P - P^e)$ *vs.* time were linear to the same high precision (about 0.2%) previously reported.[4a] The slopes, $S/2.303$, were determined by the method of least squares. Fifteen to thirty points, covering 60 to 80% reaction, were used in determining each value of S.

The rate of hydration, k_p, for gaseous olefin at unit pressure and the rate of dehydration, k_{-1}, for aqueous alcohol at unit concentration are given by the expressions (see ref. 4a for definition of symbols)

$$k_p = (r/RT + h)(S - k_{-1}) \qquad (1)$$

$$k_{-1} = \frac{P^e}{P^0}(S) \qquad (2)$$

With a knowledge of the distribution constant, h, it is possible to obtain a k_p value from a single kinetic experiment by use of eq. 1. This is in contrast to the seven or more experiments employed in a plotting procedure to determine k_p when h is unknown.[4a] The general procedure employed in this work was to make four experiments at varying r/RT under otherwise similar conditions. Rate constants, k_p, were calculated for each experiment by eq. 1 and the average k_p value taken. The precision measures are based on the deviations for the four calculated k_p values from the average. Actually the value of h used in eq. 1 need not be highly accurate if r/RT values of 0.100 or greater are employed for h is small by comparison particularly at the higher temperatures. In Table I are given typical data illustrating the calculation of k_p. Under the conditions given eight experiments were performed in order to compare the direct h method (eq. 1) and the least squares plotting method of obtaining k_p.[4a] The excellent agreement between the two methods is shown in the comparison of results given in Table I. The improved precision of the present method is also indicated.

TABLE I

TYPICAL DATA SHOWING CALCULATION OF RATE CONSTANT, k_p, AND A COMPARISON OF METHODS FOR CALCULATING, k_p. TRIMETHYLETHYLENE AT 9.70° IN 0.973 *M* NITRIC ACID

$10^3(r/RT)$	$10^3(h + r/RT)$	$10^3(S - k_{-1})$	10^5k_p (eq. 1)	d, %
19.96	31.0	1.247	3.86	0.3
22.0	33.0	1.157	3.82	1.3
34.1	45.1	0.839	3.83	1.0
49.9	60.9	.636	3.87	0.0
69.5	80.5	.483	3.89	0.5
90.9	101.9	.385	3.93	1.5
96.0	107.0	.365	3.91	1.0
99.4	110.4	.347	3.83	1.0
		Av.	3.87	0.8

COMPARISON OF METHODS

	Least squares method[4a]	Direct h method (eq. 1)
$10^5\ k_p$	3.90 ± 0.045 moles l.$^{-1}$ atm.$^{-1}$ min.$^{-1}$	3.87 ± 0.025 moles l.$^{-1}$ atm.$^{-1}$ min.$^{-1}$
$10^2\ h$	1.161 ± 0.051 moles l.$^{-1}$ atm.$^{-1}$	1.110 ± 0.008 moles l.$^{-1}$ atm.$^{-1}$

Results

The Rates of Hydration, k_p, of Gaseous Isobutene and Trimethylethylene by 0.973 *M* Nitric Acid.—A value of k_p for isobutene at 45° was obtained in the present work. This value together with those previously obtained[4a] are given in Table II.

TABLE II

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS ISOBUTENE BY 0.973 *M* NITRIC ACID IN UNITS OF 10^5 MOLE L.$^{-1}$ ATM.$^{-1}$ MIN.$^{-1}$

Temp., °C.	14.96	24.89	34.84	45.03
k_p	7.88	21.9	55.5	142
P.e.[a]	0.09	0.14	0.40	2.0

[a] Probable error, *cf.* Experimental. This notation used throughout.

The rates of hydration of gaseous trimethylethylene have been determined for the temperature interval 0–40°. The rate constants, k_p, are listed in Table III.

TABLE III

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS TRIMETHYLETHYLENE BY 0.973 *M* NITRIC ACID IN UNITS OF 10^5 MOLES L.$^{-1}$ ATM.$^{-1}$ MIN.$^{-1}$

Temp., °C.	0.00	9.70	20.00	30.00	40.00
k_p	1.424	3.87	10.21	25.8	59.4
P.e.	0.011	0.03	0.06	0.3	0.2

The hydration of isobutene under the conditions employed was slightly but measurably reversible at 45°. A reverse rate constant, k_{-1}, of 7.6×10^{-4} min.$^{-1}$ was obtained by eq. 2 under these conditions. At 35° and below the reverse reaction is unimportant in calculation of k_p values for isobutene.[4a] Only at 0.00° was k_{-1} for *t*-amyl alcohol

TABLE IV

RATE CONSTANTS, k_{-1}, FOR THE DEHYDRATION OF AQUEOUS *t*-AMYL ALCOHOL BY 0.973 *M* NITRIC ACID IN UNITS OF 10^4 MIN.$^{-1}$

Temp., °C	9.70	20.00	30.00	40.00
k_{-1}	0.07	0.30	1.38	6.60
P.e.	0.007	0.01	0.03	0.2

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[9] R. W. Taft, Jr., E. L. Purlee and P. Riesz, THIS JOURNAL, **77**, 899 (1954).

negligible. The rate constants, k_{-1}, obtained by eq. 2 at the other temperatures are listed in Table IV

The Distribution Constants, *h*, for Gaseous Isobutene and Trimethylethylene in Water and Acid Solutions.—The distribution constants for isobutene and trimethylethylene between the vapor phase and saturated aqueous solution, measured over the temperature interval 0–50°, are given in Table V.

TABLE V

DISTRIBUTION CONSTANTS, *h*, FOR ISOBUTENE AND TRIMETHYLETHYLENE BETWEEN WATER AND THE VAPOR PHASE IN UNITS OF 10^3 MOLES L.$^{-1}$ ATM.$^{-1}$

Temp., °C.	Isobutene *h*	Isobutene P.e.	Trimethylethylene *h*	Trimethylethylene P.e.
0.01	15.36	0.07	18.40	0.10
9.70	9.53	.05	11.00	.08
15.00	7.54	.06	....	..
17.05	6.86	.03	....	..
20.00	...	..	7.01	.03
25.00	5.18	.01	....	..
30.00	4.57	.05	4.89	.03
35.00	4.12	.02	....	..
40.00	3.74	.09	3.44	.01
50.00	3.12	.03	2.47[a]	.01

[a] Temp. = 49.73°.

The distribution constants for isobutene and trimethylethylene in 0.973 *M* nitric acid measured over the temperature intervals 0–25° and 0–30°, respectively, are given in Table VI.

TABLE VI

DISTRIBUTION CONSTANTS, *h*, FOR ISOBUTENE AND TRIMETHYLETHYLENE BETWEEN 0.973 *M* NITRIC ACID AND THE VAPOR PHASE IN UNITS OF 10^3 MOLES L.$^{-1}$ ATM.$^{-1}$

Isobutene

Temp., °C.	0.00	9.70	15.00	25.00
h	14.62	9.53	7.86	5.75
P.e.	0.06	0.05	0.05	0.04

Trimethylethylene

Temp., °C.	0.00	9.70	30.00
h	18.63	11.00	5.66
P.e.	0.08	0.08	0.06

Thermodynamic Rate Properties.—Plots of log k_p *vs.* $1/T$ are linear within the precision of measurement for isobutene over the temperature range 15–45° and for trimethylethylene over the range 10–40°. The points fit straight lines derived by the method of least squares with a median deviation of less than 1% as shown in Table VII. For trimethylethylene the point at 0.00° deviates from the least squares line for the 10–40° data by an amount barely outside of experimental error.

With linearity established over the indicated temperature ranges, we may use eq. 8 and 9 of reference 4a to obtain best values of the enthalpy of activation, $\Delta H_p^{\ddagger}$, and the entropy of activation, $\Delta S_p^{\ddagger}$, for the hydration of the gaseous olefins. These results are listed in Table VIII.

TABLE VIII

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE HYDRATION OF GASEOUS ISOBUTENE AND TRIMETHYLETHYLENE BY 0.973 *M* NITRIC ACID

	$\Delta H_p^{\ddagger}$, kcal./mole	P.e.,[a] kcal./mole	$\Delta S_p^{\ddagger}$, cal./deg.	P.e.,[a] cal./deg.	Temp., °C.
Isobutene	16.96	0.18	−26.6	0.3	15–45
Trimethylethylene	15.35	.14	−32.8	.2	10–40

[a] Average of the probable errors obtained from the end-points and the least squares lines.

The values listed in Table VIII are the same within the precision measurements as reported earlier.[4] In the case of trimethylethylene we have improved appreciably the precision of the values given ($\Delta H_p^{\ddagger}$ was given earlier, for example, as 15.22 ± 0.56 kcal./mole).[4b]

Thermodynamic Properties for Solution of Gaseous Isobutene and Trimethylethylene.—Plots of log *h* *vs.* $1/T$ for isobutene in water exhibit marked curvature below 25°, the slope for the 0–15° interval is much greater than that of the higher temperatures. For the 25–50° interval the plot is linear within the precision of the measurements. A plot of log *h* *vs.* $1/T$ for isobutene in 0.973 *M* nitric acid shows similar characteristics in the 0 to 25° range. The distribution constants could not be obtained under these conditions above 25° because the rate of hydration is too fast to permit reliable measurements.

For trimethylethylene in water the plot of log *h* *vs.* $1/T$ is linear within the precision of measurement over the temperature interval 20–50°. The points for this temperature range fit a straight line derived by the method of least squares with a median deviation of 0.5%. Discernible curvature (but much less marked than for isobutene) is manifest in the region around 10° and below. In 0.973 *M* nitric acid trimethylethylene gives a similar plot with appreciable curvature over the measurable range (0–30°), especially around 10°.

Mean enthalpies and entropies of solution of the gaseous olefins may be obtained by use of the equations

$$\Delta H_s = 2.303R \frac{T_1T_2}{T_2 - T_1} \log (h_2/h_1) \qquad (3)$$

$$\Delta S_s = (2.303R) \left[\frac{T_2 \log h_2 - T_1 \log h_1}{T_2 - T_1}\right] \qquad (4)$$

TABLE VII

LEAST SQUARES FIT OF LOG k_p *vs.* $1/T$ FOR ISOBUTENE AND TRIMETHYLETHYLENE

Temp., °C.	10^5k_p obsd.	10^5k_p calcd.	*d*, %	Temp., °C.	10^5k_p obsd.	10^5k_p calcd.	*d*, %
14.96	7.88 ± 0.09	7.87	0.1	9.70	3.87 ± 0.04	3.86	0.5
24.89	21.9 ± .1	21.8	0.5	20.00	10.21 ± .06	10.33	1.2
34.84	55.5 ± .4	56.4	1.1	30.00	25.8 ± .3	25.6	0.8
45.03	142 ± 2.0	141	0.7	40.00	59.4 ± .2	59.6	.3
		Av.	0.7			Av.	0.7
				0.00	1.424 ± .011	1.386	2.7

T_2 and T_1 represent the highest and lowest temperatures, respectively, of the temperature interval employed. The corresponding distribution constants are h_2 and h_1, respectively.

Table IX lists mean enthalpies of solution of isobutene and trimethylethylene in water for a series of small temperature intervals covering the range 0 to 50° which illustrate the relationships discussed above. The last temperature interval listed in each case is for the wide range in which the enthalpies of solutions are essentially temperature independent. Table X lists similar results for solution in 0.973 *M* nitric acid.

Above 10° the distribution constants for these olefins in water and in 0.1 *M* nitric acid have been found to be experimentally indistinguishable.[9] Thus the thermodynamic properties for the solution of olefin in water may be applied for solution in 0.1 *M* acid. The thermodynamic properties of solution in 1 *M* nitric acid and in water are, however, clearly not equivalent—see Tables IX and X. Fortunately, for the comparison of the thermodynamic properties for the two olefins, the relative enthalpy and entropy of solution (of trimethylene referred to isobutene) are the same within experimental error in water and one molar acid. For the temperature interval 10 to 25 or 30°, the difference between the enthalpy of solution in one molar acid and water is 1.15 ± 0.2 kcal. for isobutene, and that for trimethylethylene is 1.12 ± 0.2 kcal. (Tables IX and X).

TABLE IX

MEAN ENTHALPIES OF SOLUTION OF GASEOUS ISOBUTENE AND TRIMETHYLETHYLENE IN WATER

Temp. interval, °C.	Mean ΔH_s, kcal./mole	P.e.	Temp. interval, °C.	Mean ΔH_s, kcal./mole	P.e.
	Isobutene			Trimethylethylene	
0–10	−7.56	0.11	0–10	−8.13	0.14
10–25	−6.68	.15	10–20	−7.21	.14
20–30	−5.50	.10	10–30	−6.80	.14
25–35	−4.18	.09	20–30	−6.36	.14
40–50	−3.74	.53	30–40	−6.64	.13
25–50	−3.87	.04	40–50	−6.84	.20
			20–50	−6.56	.05

TABLE X

MEAN ENTHALPIES OF SOLUTION OF GASEOUS ISOBUTENE AND TRIMETHYLETHYLENE IN 0.973 *M* NITRIC ACID

Temp. interval, °C.	Mean ΔH_s, kcal./mole	P.e.	Temp. interval, °C.	Mean ΔH_s, kcal./mole	P.e.
	Isobutene			Trimethylethylene	
0–10	−5.53	0.09	0–10	−8.13	0.14
10–25	−6.77	.12	10–30	−5.58	.10

Thermodynamic Properties of the Hydration of Dissolved Isobutene and Trimethylethylene.—The relationships between the rate of hydration, k_p, of gaseous olefin at unit pressure and the rate of hydration, k_c, of dissolved olefin at unit concentration and corresponding rate thermodynamic quantities, are given by the equations

$$k_c = k_{p/h} \tag{5}$$

$$\Delta H^{\ddagger}_{c} = \Delta H^{\ddagger}_{p} - \Delta H_s \tag{6}$$

$$\Delta S^{\ddagger}_{c} = \Delta S^{\ddagger}_{p} - \Delta S_s \tag{7}$$

The temperature independence of $\Delta H^{\ddagger}_{p}$ (as discussed above) requires by these relationships that $\Delta H^{\ddagger}_{c}$ and $\Delta S^{\ddagger}_{c}$ exhibit a temperature dependence paralleling that of ΔH_s and ΔS_s. In the case of isobutene this becomes marked in the lower temperature region. Thus the heat capacity of the ionic hydration transition state must be very close to that for the corresponding gaseous olefin and aqueous acid but not that of the dissolved olefin, the latter holding particularly for isobutene.

From the values of $\Delta H^{\ddagger}_{p}$ and $\Delta S^{\ddagger}_{p}$ for isobutene (applying to 0.0909 *M* nitric acid) given in reference 4a, the thermodynamic quantities listed in Table XI are obtained. These values are to be directly compared with the values of $\Delta H^{\ddagger}_{c}$, 22.8 kcal. and $\Delta S^{\ddagger}_{c}$, −2 e.u. obtained from the data reported by Lucas and Eberz for the interval 25–35°. Virtually equivalent values have been also reported by Ciapetta and Kilpatrick under the same conditions.[10] The agreement between the latter values and those of Table XI is considered as good as is warranted by the combined precision of our results and particularly the uncertainties of the methods of measurement employed by the above investigators. Lucas and Eberz's method involved the titration of volatile olefin while Ciapetta and Kilpatrick made dilatometric measurements with this volatile reactant. In both these cases the thermodynamic quantities have been derived from rate measurements only 10° apart. Thus appropriately distributed errors of 4% in the rate constants at 25 and 35° can account for the discrepancies (*cf.* Appendix).

TABLE XI

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE HYDRATION OF DISSOLVED ISOBUTENE BY 0.0909 *M* NITRIC ACID

Temp. interval, °C.	$\Delta H^{\ddagger}_{c}$, kcal./mole	P.e., kcal./mole	$\Delta S^{\ddagger}_{c}$, cal./deg.	P.e., cal./deg.
15–25	23.7	0.3	+0.8	0.6
25–35	21.5	.2	−6.7	.7
25–50	21.1	.2	−7.7	.7

Although measurements of rates with trimethylethylene have not been made under the same acidity as used by Lucas and Liu (0.1 *M* nitric acid), it is possible from our measurements to obtain values for enthalpies and entropies of activation which apply to these conditions. Thus use may be made of the fact (see above section) that the relative enthalpies and entropies of solution of trimethylethylene in 0.1 and 1 *M* acid are equal. This, together with the reasonable assumption that the relative enthalpies and entropies of activation for the hydration of gaseous trimethylethylene at these two acidities may also be taken equal within the precision of measurement,[11] lead to the values of the enthalpy, $\Delta H^{\ddagger}_{c}$, and entropy, $\Delta S^{\ddagger}_{c}$, of activation for the hydration of dissolved trimethylethylene by 0.1 *M* nitric acid given in Table XII.

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

[11] This is supported by the equivalence of the effect of acidity on the hydration rates of these (and other) olefins, R. W. Taft, Jr., *et al.*, *ibid.*, **77**, in press (1955).

TABLE XII

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE HYDRATION OF DISSOLVED TRIMETHYLETHYLENE BY 0.1 *M* NITRIC ACID

Temp. interval, °C.	$\Delta H_c^\ddagger$, kcal./mole	P.e., kcal./mole	$\Delta S_c^\ddagger$, cal./deg.	P.e., cal./deg.
25–50[a]	22.2	0.3	−5.1	0.9

[a] The values given apply also to the temperature interval 25–35°.

Lucas and Liu give results which lead to values of $\Delta H_c^\ddagger$, 18.4 kcal./mole and $\Delta S_c^\ddagger$, −18.9 e.u. The discrepancy between these and the present values is very serious. In accounting for the source of the difficulty, we note that Lucas and Liu report a sharp falling off of the initial first-order rate of hydration starting at about 40% reaction (this is in contrast to the isobutene work of Lucas and Eberz in which linear plots of log (c_0/c) *vs.* time were obtained). Lucas and Liu attributed these results to an interfering polymerization. In the present work strictly linear first-order plots were observed in all cases. It seems possible that the presence of peroxides which were not excluded by the method of Lucas, *et al.*, might have been responsible. Further, the smaller concentration of dissolved olefin employed in our experiments (about one-twentieth that used by Lucas and Liu) may have helped to eliminate polymerization which may occur at higher olefin concentrations. In our measurements loss of volatile reactant and the presence of peroxides was eliminated by operating in closed evacuated systems, the olefin being vaporized into the system to start reaction (*cf.* Experimental). As with isobutene, the enthalpies and entropies of activation for trimethylethylene from Lucas and Liu's work are derived from rate constants only 10° apart.

Discussion

The enthalpy of activation for the hydration of dissolved trimethylethylene relative to that for isobutene by dilute nitric acid is close to +1.3 kcal., instead of the value of −4.4 kcal. reported earlier by Lucas and co-workers. At 25° the rate of hydration of trimethylethylene is 0.67 times that of isobutene as indicated (approximately) earlier by Lucas, *et al.* This illustrates that the present finding of serious errors in the activation energies reported by Lucas, *et al.*, in no way detracts from the principal conclusions concerning rate relationships reached in these fine preliminary studies of the olefin hydration reaction. It is hoped that the present results will serve as a useful warning to those who are unaware or take too lightly the inherent experimental difficulty of determining energies of activation of sufficient precision. It is not uncommon to find theoretical interpretations of differences in enthalpies of activation given for cases where the nature of the experimental data indicate that it is quite likely that this quantity is only experimental error.[12] The danger of attempting to derive useful relative enthalpies of activation from any but the most accurate of rate data (*ca.* 1%) taken only 10° apart has been adequately demonstrated here. Even when the precision of the data justifies such a procedure, one cannot be certain without further study that the values obtained are sufficiently temperature insensitive to apply outside the small temperature interval employed.[13] This matter is of importance in studies of the effect of structure on free energy and enthalpy of activation, for in a series where rates vary widely it is seldom possible to obtain the enthalpies for each compound for the same temperature interval.

The relative thermodynamic rate properties for the hydration of trimethylethylene (with isobutene as standard of comparison) obtained in this work are summarized in Table XIII.

TABLE XIII

RELATIVE THERMODYNAMIC RATE PROPERTIES FOR THE HYDRATION OF TRIMETHYLETHYLENE BY 0.973 *M* NITRIC ACID

Isobutene is the Standard of Comparison

k_p/k_{p0} 25°	$\Delta\Delta H_p^\ddagger$, kcal./mole	$\Delta\Delta S_p^\ddagger$, cal./deg.	k_c/k_{c0}, 25°	$\Delta\Delta H_c^\ddagger$, kcal./mole	$\Delta\Delta S_c^\ddagger$, cal./deg.
0.71	−1.61 ± 0.32	−6.2 ± 0.4	0.67	+1.1 ± 0.3	+2.6 ± 0.5

In solution, there is considerable presumption that the relatively small effect of change in olefin structure on rate is a consequence of compensating larger effects on the enthalpy and entropy of activation since the results reported for the latter (*cf.* Table XIII) are about four times the estimated probable errors.

Price and Hammett have proposed a principle to the effect that in a polar reaction the more complex (entropy containing) molecule loses more in entropy in attaining the activated state.[14] The principle is nicely illustrated by the relative entropy of the trimethylethylene hydration transition state, $S^\ddagger - S_0^\ddagger$. This quantity may be obtained by combining the relative entropy and the relative entropy of activation of the gaseous olefin according to the relationship

$$S^\ddagger - S_0^\ddagger = (\Delta S_p^\ddagger - \Delta S_{p0}^\ddagger) + S^0(g) - S_0^0(g) \quad (8)$$

$S^\ddagger$ refers to the standard absolute entropy of the hydration transition state, $S^0(g)$ to the standard absolute entropy of gaseous olefin, and the subscript zero refers to the standard of comparison, isobutene. In this manner a value for $(S^\ddagger - S_0^\ddagger)$ for the trimethylethylene transition state of +4.5 ± 0.5 e.u. is obtained, which is 6.2 e.u. less than the difference in the entropies of the gaseous reactants (*i.e.*, $S^0(g) - S_0^0(g) = +10.7$ e.u.).[15] In the present reactions, however, our data show (*cf.* Table XIII) that all of (in fact more than) this entropy loss takes place on simply transferring the olefins from the vapor state to aqueous solution. Thus the Price and Hammett rule is followed by the hydration of these gaseous olefins at unit pressure but not by that for the dissolved olefins at unit concentration.

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(12) *Cf.* Appendix.

(13) V. K. LaMer, *J. Chem. Phys.*, **1**, 289 (1933).

(14) F. P. Price, Jr., and L. P. Hammett, THIS JOURNAL, **63**, 2387 (1941).

(15) (a) Ref. 6a, p. 217; (b) ref. 6b.

Appendix

Errors in Activation Enthalpies and Entropies.—The Arrhenius activation energy is given by

$$\Delta E_a = \frac{RT_1T_2 \ln (k_2/k_1)}{T_2 - T_1}$$

Consider the errors (or precision measures) of k_2 and k_1 as $\pm r_2$ and r_1, respectively. Then

$$\ln (k_2 \pm r_2) = \ln \left[k_2 \left(1 \pm \frac{r_2}{k_2}\right)\right]$$

but r_2/k_2 is small compared to one so

$$\ln (k_2 \pm r_2) = \ln k_2 \pm r_2/k_2$$

and similarly for k_1 and r_1. Thus the Arrhenius activation energy becomes

$$\Delta E_a = \frac{RT_1T_2}{T_2 - T_1} \ln (k_2/k_1) \pm \frac{RT_1T_2}{T_2 - T_1} [(r_2/k_1)^2 + (r_1/k_2)^2]^{1/2}$$

The second term in this equation is the statistical error in the activation energy. Consider, for example, the temperature interval 25–35°. The term $RT_1T_2(T_2 - T_1)$ has the numerical value of 18,260 cal. mole^{-1} and thus errors of 1% in both k_2 and k_1 will lead (irrespective of the values of k_2 and k_1) to errors in ΔE_a of ±256 cal. mole^{-1}. Two per cent. errors in both k_2 and k_1 lead to twice as great an error in ΔE_a (±512), 3% three times (±768), etc. The error may be decreased by increasing the temperature interval (provided the Arrhenius eq. is followed). Thus a 20° interval instead of a 10° interval (at about the same mean temperature) will give essentially half the error, a 30° interval one-third, etc. It is to be noted that the statistical error does not give the maximum error. Thus in the example cited above appropriately distributed errors of 1% will lead to a maximum error of ±365 cal. mole^{-1}. In as much as it is not uncommon to find rate data reported in the literature as accurate to 5%, it is apparent from this discussion that differences in energies of activation obtained from a 10° interval (near room temperature) are commonly insignificant (*i.e.*, within experimental error) unless greater than 1.5 kcal. The inherent difficulty in obtaining precise enthalpies of activation is particularly well emphasized when one considers that if other factors were equal this 1.5 kcal. factor would introduce better than one power of ten difference in rates. The entropy of activation and its statistical error is given by

$$\Delta S^{\ddagger} = \frac{RT_2 \ln k_2 - RT_1 \ln k_1}{T_2 - T_1} - R \ln \frac{kT}{h} - R \pm \frac{R}{T_2 - T_1} \sqrt{\left(T_2 \frac{r_2}{k_2}\right)^2 + \left(T_1 \frac{r_1}{k_1}\right)^2}$$

The above discussion applies as well to equilibrium constants, enthalpy and entropy changes and their errors.

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The Photolysis of Acetaldazine

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The products of the photolysis of acetaldazine have been investigated at 30, 100 and 170°, over the wave length region 3340 to 2380 Å. These products listed in order of their importance are acetonitrile, ammonia, nitrogen, methane, ethane and 2-butene. In order to explain the variation of the quantum yields with experimental conditions it is necessary to propose several primary mechanisms, the two most important being $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow CH_3CN + CH_3CH{=}NH$ (2), $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow CH_3 + CH{=}N{-}N{=}CHCH_3$ (3). The large amounts of acetonitrile ($\Phi \sim 0.5$ at longer wave lengths) are apparently formed exclusively by (2) along with ethylidineimine which evidently forms a linear type addition polymer capable of liberating part of its nitrogen as ammonia either in the system or at the low pressures used in the collection procedures. The methyl radicals liberated in (3) may abstract hydrogen atoms from the azine to form methane, combine to form ethane, or initiate a radical polymerization by addition to the conjugated azine molecule. The 2-butene and some of the nitrogen produced must be the result of $CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \rightarrow N_2 + CH_3CH{=}CHCH_3$ although the nitrogen is always considerably in excess of the 2-butene and appears to be a product of some radical reaction especially at high temperatures.

The Photolysis of Acetaldazine.—Evidence that the ethylidene biradical, CH_3CH, enters into the thermal and photochemical decomposition mechanism of diazoethane has been given in two previous papers.[1,2] Since it is probable that isomerization is slow enough to allow formation of 2-butene by a radical combination reaction, a more detailed study of the reactions of the ethylidene radical would be of interest. Inasmuch as considerable difficulty was encountered with the unstable and sometimes explosive diazoethane, another means of generating ethylidene radicals would be desirable. Such a possibility is suggested by the photolysis of acetaldazine if a primary step such as

$$CH_3CH{=}N{-}N{=}CHCH_3 + h\nu \longrightarrow 2CH_3CH + N_2 \qquad (1)$$

occurs. Although this reaction is no more than 30 kcal. endothermic, several preliminary photolyses showed that it did not occur to any appreciable extent. The main decomposition products were identified as acetonitrile and ammonia. In view of these unexpected results the study of the photolysis of acetaldazine was carried out in some detail.

Experimental

Acetaldazine was prepared from acetaldehyde and hydrazine hydrate according to the method described by

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(1) D. H. Volman, P. A. Leighton, F. E. Blacet and R. K. Brinton, *J. Chem. Phys.*, **18**, 203 (1950).

(2) R. K. Brinton and D. H. Volman, *ibid.*, **19**, 1394 (1951).