These are in good agreement with the values of 19 and 20 kcal.[21,22] found by previous workers.[23]

The present work does not provide a means of deciding which hydrogen atom is abstracted from the ketone in reaction (4). By analogy with methyl radical reactions[19] it is most probable that the abstraction occurs in either the α- or β-position to the carbonyl group. At high temperatures, however, the possibility of abstraction in the γ-position must be considered. If this occurred, the resulting heptanonyl radical might be expected to yield, on decomposing, the trimethylene biradical. It has been shown[24] that this radical may undergo ring closure in the gas phase to form cyclopropane. The presence of cyclopropane was therefore sought in the products of a run at 357°. Mass spectrometer analysis, however, showed that this compound was not formed in detectable amount, thus providing indirect evidence that the value of 6.5 kcal. found for E_4 refers to secondary hydrogen abstraction.

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[21] R. W. Durham, G. R. Martin and H. C. Sutton, *Nature*, **164**, 1052 (1949).

[22] S. Bywater and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 319 (1951).

[23] Note added in revision: These values for E_3 indicate a high value for the C–H bond strength in propane (ref. 22). This is in agreement with recent findings by C. H. Leigh and M. Szwarc, *ibid.*, **20**, 407 (1952), and by D. P. Stevenson (quoted in Leigh and Szwarc).

[24] C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates, Equilibrium and Temperature Coefficients in the Reversible Hydration of Gaseous 1-Methylcyclopentene-1 by Dilute Nitric Acid[1]

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The rate of hydration to 1-methylcyclopentanol-1 of 1-methylcyclopentene-1 by dilute aqueous nitric acid is 3.64 times faster at 35° than is that of isobutene to *t*-butyl alcohol, and 3.05 times faster at 45°. The enthalpy of activation for the cyclic olefin is 3.50 ± 0.27 kcal. less than that of isobutene, the entropy of activation is 9.0 ± 0.9 cal./deg. less. The small difference in rate between the two olefins arises therefore from a difference in entropy of activation which almost completely compensates a difference in enthalpy of activation which would by itself make the reaction of the cyclic compound 300 times faster than that of isobutene. The reaction of the methylcyclopentene is considerably less complete than is that of isobutene, and precise values for the rate of dehydration of the alcohol and for the equilibrium constant have been obtained. The dehydration has an unusually high temperature coefficient and a positive entropy of activation, 9.6 ± 0.8 cal./deg.

We have studied the reversible conversion of 1-methylcyclopentene-1 in the gas phase to 1-methylcyclopentanol-1 dissolved in dilute aqueous nitric acid both by "hydration" measurements, *i.e.*, measurements starting from the gaseous olefin, and by "dehydration" measurements, which start from the dissolved alcohol. Although the hydration of this olefin, in contrast to that of isobutene,[2] is markedly reversible, the equations and procedures used in article I for computing the specific rates from experimental data on the rate of the drop in pressure apply without alteration to the present hydration measurements.

Our treatment of the dehydration case is based upon the considerations which follow. We use the same symbols as in article I, namely: P = partial pressure of olefin at time t; C_a = concentration of alcohol at time t; P^0, C_a^0 and P^e, C_a^e are corresponding values at time 0 and at equilibrium, respectively; r = (volume of gas phase)/(volume of solution); h = distribution constant C/P of olefin between phases; k_p = rate of conversion of olefin to alcohol at unit pressure of olefin; k_{-1} = rate of conversion of alcohol to olefin at unit concentration of alcohol. The basic relation, eq. (I-1), of article I still applies but the material balance relation, eq. (I-2), is replaced by

$$C_a = C_a^0 - P(h + r/RT) \qquad (1)$$

By manipulations which parallel those of article I one can obtain the relation

$$s \equiv -\frac{\mathrm{d}\ln(P^e - P)}{\mathrm{d}t} = \frac{k_p}{h + r/RT} + k_{-1} \qquad (2)$$

which differs from eq. I-5 of the hydration case only in the replacement of $P - P^e$ by $P^e - P$. By eliminating the quantities k_p and C_a^0 between eq. 2, I-4, and the relation

$$C_a^e = C_a^0 - P^e(h + r/RT) \qquad (3)$$

which is an obvious corollary of eq. (1), one gets

$$\frac{C_a^0 RT}{sP^e r} = \frac{1}{k_{-1}} + \frac{h}{k_{-1}}\frac{RT}{r} \qquad (4)$$

If then a series of measurements of the slope are made with varying values of the ratio r of the volumes of gas and liquid, and if the initial concentration C_a of alcohol and the equilibrium partial pressure P^e of olefin are determined in each case the value of k_{-1} can be obtained as the reciprocal of the intercept of a plot of the left side of eq. (4) against

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[1] The work reported herewith was carried out as project NR 956-062 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] J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951). This will be referred to as article I, and the equations in it will be referred to as eq. (I-1), etc. The sign of the second term on the right of eq. (I-7) was incorrectly transcribed, and the equation should read

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

$1/r$. With k_{-1} known k_p can be obtained from the intercept of a plot of the left side of the equation

$$\frac{RT}{r(s - k_{-1})} = \frac{1}{k_p} + \frac{h}{k_p}\frac{RT}{r} \qquad (5)$$

against RT/r as in the hydration case.

In general the validity of these various equations is exhibited by the precision measures quoted in Tables I and II for the values of k_p and k_{-1}. These are the probable errors in these quantities as they are obtained in the least squares treatment of the experimental data by eq. (I-7), (I-6), (4) and (5).

More particularly, we have in no case observed any systematic curvature in plots of log $(P - P^e)$ against time for the hydration or in plots of log $(P^e - P)$ for the dehydration. In a typical hydration experiment in which the total variation in log $(P - P^e)$ was 0.64 the maximum deviation from the best straight line was 0.008 and the median deviation was 0.0022. In a typical dehydration run in which log $(P^e - P)$ varied by 0.65 the maximum deviation was 0.007 and the median deviation was 0.0021. These precision measures are closely the same as those observed in the hydration of isobutene.

In 11 hydration experiments at a single temperature in which $10^3\ s$ varied from 4.6 to 9.3 the average deviation between observed values of s and those computed from eq. (I-7) was 1.2%. For 12 dehydration experiments in which $10^3\ s$ varied from 4.1 to 6.7 the average deviation between observed values of s and those computed from eq. (4) was 1.0%. For 11 hydration runs in which $10^3\ s$ varied from 0.91 to 1.99 the maximum deviation of the computed value of k_{-1} from the mean was 5% and the average deviation 2%.

The close agreement between the values of the specific rates derived from the hydration and from the dehydration experiments is further evidence for the validity of the method and the precision of the results. It also rules out the possibility that any appreciable isomerization of either olefin or alcohol occurs during the course of the measurements.

Experimental

Apparatus.—The apparatus of article I was used. For the dehydration measurements the reaction flasks used for olefin hydration were modified by the inclusion of a side tube P' and an internal cylindrical compartment of 10-ml. capacity directly below tube P and by increasing the total volume to 50 ml. The geometry of the dehydration apparatus permitted a range of r/RT values from about 0.04 to 0.14 l.$^{-1}$ atm.$^{-1}$. All of the data were obtained at a shaking rate (frequency of oscillation of the reaction flask) of 350 r.p.m. or slightly greater. In article I this was shown to be adequate to meet the required distribution equilibrium of olefin between gas and liquid.

Hydration Procedure.—Procedure B of article I was used, except that the olefin was introduced into the system as in procedure A. The part of the apparatus comprising the reaction system with nitric acid solution in the reaction flask and the part containing a tube with several drops of liquid olefin (see Fig. 1 in article I) were each degassed three times, as previously described, and the apparatus completely immersed in a thermostat at the temperature at which the reaction was to be run. Stopcock S was opened, allowing olefin to evaporate into the reaction system until the manometer reading was near the vapor pressure of olefin. S was then closed, the apparatus was quickly removed from the thermostat, care being taken to prevent agitation, and the contents of the reaction flask were frozen by immersing in a Dry Ice–carbon tetrachloride-chloroform-bath. The system was evacuated to 0.5 mm. and sealed off at L. With the contents of the reaction flask frozen, the apparatus was placed in the thermostat and allowed to come to near bath temperature without agitation, and the shaking was then started (this was taken as zero time). Since reactions were slow, errors introduced in the zero time were so small that $P°$ values of satisfactory precision could be obtained. All reactions were followed to at least two-thirds of the pressure drop to equilibrium. Equilibrium pressures were obtained as in article I.

Dehydration Procedure.—A desired volume of an aqueous solution of 1-methylcyclopentanol-1 was introduced from a calibrated buret *via* a small pipet through P of Fig. 1 into the inner cylindrical compartment. Similarly, nitric acid solution was introduced through P' into the outer compartment, the reaction flask being rigidly mounted to prevent mixing of the two solutions. P and P' were sealed off, the system was degassed twice as previously described, and, after the last freezing, evacuated to 0.5 mm. pressure and sealed at L. With the contents of the reaction flask frozen, the apparatus was immersed in the thermostat and allowed to come to near bath temperature, and shaking was then started. With the rapid and vigorous shaking provided, the alcohol and acid solutions became uniformly mixed and came to bath temperature within a very few minutes. Volumes and concentrations of alcohol and nitric acid were chosen to give reaction mixtures of 0.0909 molar in nitric acid and 0.0523 molar (at 20°) in the alcohol. Reactions were followed as described under Hydration Procedure. The volume per cm. of P and P' was 0.12 ml., and volumes in these sections above and below the calibration mark (Vg and Ve were determined as previously) were accounted for by measuring these heights.

Temperatures were controlled to ±0.02°, and measured with a thermometer calibrated by the Bureau of Standards. Times were measured to ±0.05 minutes.

Solvent Pressures.—The values of Ps, the partial pressure of the solvent, were determined at each of the required temperatures for each apparatus by using the same procedure as for carrying out an experiment except that olefin and alcohol were omitted.

Materials.—1-Methylcyclopentanol-1 was prepared by treating cyclopentanone with $MgCH_3Br$. The crude product was carefully purified by repeated sublimations. The material used for the kinetic work had a m.p. 34.8–35.3°. Timmermans and Hennaut-Roland[3] give m.p. 35.50°.

1-Methylcyclopentene-1 was prepared by dehydration of 1-methylcyclopentanol-1.[3] The material used in the kinetic work was a middle cut in a careful fractionation of the crude product and had b.p. 75.2–75.6° (uncor.) (760 mm.), n^{23}_D 1.4287. Literature values[3] for these constants are b.p. 75.85° (760 mm.), n^{15}_D 1.4352.

Results and Discussion

The specific rates obtained are tabulated in Tables I and II along with the probable errors which measure their precision.

TABLE I

Specific Rates, k_p, in 10^5 mole-l.$^{-1}$-atm.$^{-1}$-min.$^{-1}$ for the Hydration of Gaseous 1-Methylcyclopentene-1 in 0.0909 *m* Nitric Acid

Temp., °C.	k_p from hydration	k_p from dehydration
29.89	7.41 ± 0.07	....
34.84	11.00 ± .20	11.29 ± 0.18
44.92	23.0 ± .38	23.1 ± .37

TABLE II

Specific Rates, k_{-1}, in 10^4 min.$^{-1}$ for the Dehydration of Aqueous 1-Methylcyclopentanol-1 in 0.0909 *m* Nitric Acid

Temp., °C	k_{-1} from dehydration	k_{-1} from hydration
29.84	....	2.35 ± 0.04
34.84	5.09 ± 0.07	5.16 ± .08
44.92	22.7 ± .18	23.2 ± .4

The relatively narrow range of temperatures over which measurements could be made was fixed on

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[3] Timmermans and Hennaut-Roland, *J. chim. phys.*, **34**, 693 (1937).

the one hand by the vapor pressure of the olefin, which became too small at lower temperatures, and on the other by the nearly complete irreversibility of the dehydration process at higher temperatures. Even so values of enthalpy and entropy of activation which are of useful precision may be computed from the data. These are reported in Table III. The precision measures are probable errors computed from the probable errors in the values of the specific rates.

TABLE III

Enthalpy $\Delta H^{\ddagger}$ and Entropy $\Delta S^{\ddagger}$ of Activation for Hydration of Gaseous 1-Methylcylopentene-1 and for Dehydration of 1-Methylcylopentanol-1 in 0.0909 *m* Nitric Acid.

	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, cal./deg.
Hydration	13.77 ± 0.24	−40.2 ± 0.8
Dehydration	28.19 ± .24	+ 9.6 ± .8

With data for three temperatures available the computation of enthalpy and entropy of activation used only the extreme temperatures. That $\Delta H^{\ddagger}$ is essentially constant over the range is shown by the computation of the specific rates at the intermediate temperature 34.84° on the basis of this constancy. For k_p the value thus computed is 10.92 ± 0.21, whereas the observed values were 11.00 ± 0.20 from hydration and 11.29 ± 0.18 from dehydration measurements. For k_{-1} the computed value is 5.11 ± 0.09, and the observed values are 5.16 ± 0.08 and 5.09 ± 0.07.

Relative Rates of Hydration of Gaseous Methylcyclopentene and Isobutene.—Comparing the data of this paper with those of article I, we find that gaseous 1-methylcyclopentene-1 hydrates in 0.0909 *m* nitric acid 3.64 times faster at 35° than does isobutene, and that the ratio is 3.05 at 45°. The enthalpy of activation of the cyclic olefin is 3.50 kcal. less than that of isobutene with a probable error of 0.27, and the entropy of activation is lower by 9.0 cal./deg. with a probable error of 0.9. If the convenient assumption frequently made that entropies of activation are independent of structure were valid, two substances whose enthalpies of activation differ by 3.5 kcal. would have rates differing by a factor of 300 instead of by something over 3. We have therefore the striking situation in which a change in structure has caused a minor change in rate of reaction only because a major change in enthalpy has been nearly compensated by a parallel change in entropy of activation.

Parallel changes in enthalpy and entropy of this sort have often been reported[4] although it is rare that such large changes cancel so completely as in the present case. The reality of the effect is always open to a certain suspicion because when two substances react at nearly the same rate an error in the determination of the temperature coefficients of the reaction rates results in the appearance of a parallel change in enthalpy and entropy.[5] It seems highly improbable that the effect is of this spurious nature in the present case for the entropy difference between the two reactions is ten times larger than its probable error.

There are indications that in the present situation the parallelism in the changes in enthalpy and entropy of activation derives largely from the fact that a larger molecule loses more both in enthalpy and in entropy in the transfer from the gas state to the condensed phase than does a smaller one. We do not have thermodynamic data on 1-methylcyclopentene-1 but the enthalpy change in the condensation to the liquid state of gaseous methylcyclopentane at 25° is 3.00 kcal. more negative than is that for isobutane, while the entropy change is 4 cal./deg. more negative for the cyclic compound.[6]

With respect to the effect of structure on entropy of activation the present reaction resembles another one in which also the transition state is highly polar[7] and in which the more complex molecule, which has the more entropy, loses more entropy in the formation of the transition state. The entropy of gaseous methylcyclopentane is 10.8 cal./deg. greater than that of isobutane,[6] and the entropy of the gaseous cyclic olefin must therefore lie not far from 11 cal./deg. higher than that of isobutene. Since we find that the former loses 9 cal./deg. more entropy in the formation of the transition state than the latter, it follows that practically all of the extra entropy possessed by the cyclic compound is lost in the conversion to the transition state of the hydration reaction.

Data on the Equilibrium. The Equilibrium Constant of the Reaction.—Methylcyclopentene(g) + H_2O(l) $\rightleftarrows$ methylcyclopentanol(aq) in mole-l.$^{-1}$-atm.$^{-1}$ is 0.315 at 29.84° and 0.1013 at 44.92°. The enthalpy change ΔH is −14.34 ± 0.34 kcal., and the entropy change ΔS is −49.8 ± 1.1 cal./deg., both figures holding for the neighborhood of 35°.

The Distribution Constant.—As in the isobutene case our data lead only to order of magnitude values for the distribution constant *h* of the olefin between gas phase and solution. The observed value is 11.7 at 30°; it is 9.5, 14.2 or 14.5 at 35°; and 3.0, 7.0 or 4.1 at 45° all in units of 10^3 mole-l.$^{-1}$-atm.$^{-1}$. The three values at the higher temperatures come, respectively, from the computation of k_p in the hydration reaction, from that of k_{-1} in the dehydration reaction, and from that of k_p in the dehydration reaction.

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(4) *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 122–123.

(5) A case where the entropy and enthalpy changes are certainly parallel is that reported by G. E. K. Branch and A. C. Nixon, THIS JOURNAL, **58**, 2499 (1936).

(6) "Selected Values of the Properties of Hydrocarbons," Circular of The National Bureau of Standards C461.

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