N'-methylthiourea. *Anal.* 0.888 mμc./mg. C., cor. for inactive carbon (3 runs).

Degradation of Propionic Acid-1,2,3-C_1^{14}.[39]—*Anal.* Found: CO_2, 0.583 mμc./mg. C. (4 runs).

The ethylamine produced from one of the runs was converted to N-phenyl-N'-ethylthiourea. *Anal.* Found: 1.10 mμc./mg. C., cor. for inactive carbon.

Acetic acid made from the ethylamine was degraded. *Anal.* Found: CO_2, 0.764 mμc./mg. C.

The methylamine produced was assayed as N-phenyl-N'-methylthiourea. *Anal.* Found: 1.46 mμc./mg. C., cor. for inactive carbon.

Processing of Acetamide-C_1^{14}; Addition of Carrier D Series.—A sample of acetamide (37.150 g.) received an irradiation of 5174 megawatt hours; acetamide survival, 65 ± 3%. *Anal.* Found: 11.86 mμc./mg. C. Total activity produced, 0.179 mc. The carriers (9.0128 g. of propionamide, 9.0413 g. of propionic acid) were added to 26.428 g. of irradiated acetamide. The mixture was homogenized by liquefaction.

Acetic Acid-C_1^{14}.—Hydrolysis of the mixture with base, isolation of the acids and fractionation of the acids was carried out as previously described under Acetic acid-C_1^{14}, A series (no mesitylene chaser was used).

Acetic acid, b.p. 118.5–119.5°, was further purified by V.P.C. The column previously described was used. The liquid phase was 90% D.C. 710 plus 10% stearic acid. A heart cut of the acetic acid was taken. This material was converted to thallous acetate and subsequently purified. *Anal.* Found: 0.811 mμc./mg. C.

Propionic Acid-C_1^{14}.—Propionic acid, b.p. 140.5–141.1°, from the fractionation of the acid fraction was purified by V.P.C. as described under acetic acid-1,2-C_1^{14}. The heart cut of this material was converted to thallous propionate and subsequently purified. *Anal.* Found: 0.886 mμc./mg. C.

Degradation of Acetic Acid-1,2-C_1^{14}.—The thallous salt was degraded. *Anal.* Found: CO_2, 0.991 mμc./mg. C.

The methylamine was assayed as N-phenyl-N'-methylthiourea. *Anal.* Found: 0.608 mμc./mg. C., cor. for inactive carbon.

Degradation of Propionic Acid-1,2,3-C_1^{14}.—The thallous salt was degraded. *Anal.* Found: CO_2, 0.644 mμc./mg. C.

The ethylamine was assayed as N-phenyl-N'-ethylthiourea. *Anal.* Found: 0.959 mμc./mg. C., cor. for inactive carbon.

Acetic acid made from the ethylamine was degraded. *Anal.* Found: CO_2, 0.646 mμc./mg. C.

The methylamine produced was assayed as N-phenyl-N'-methylthiourea. *Anal.* Found: 1.32 mμc./mg. C., cor. for inactive carbon.

UPTON, NEW YORK

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Rate of Hydration of Methylenecyclobutane and the Effect of Structure on Thermodynamic Properties for the Hydration of Small Ring Olefins[1]

BY PETER RIESZ, ROBERT W. TAFT, JR., AND ROBERT H. BOYD

RECEIVED FEBRUARY 4, 1957

The effects of small ring structure on the position of equilibrium in hydration of olefins to *t*-carbinols have been found to be of substantial magnitude and in the directions predicted by Brown's I-strain rules. The relatively small effects of ring size on the rates of hydration which are found indicate that there is no appreciable covalent bonding of a water molecule to carbon in the reaction transition state. It is concluded from the observed effects of structure on the rate of hydration that the π-complex provides a more suitable model for the molecular structure (nuclear arrangement) of the transition state than does the classical carbonium ion. The transition state exhibits the property of possessing carbonium ion character with respect to electronic, but not molecular, structure. This property is attributed to more sluggish nuclear than electronic rearrangements in attaining the transition state.

The rates of hydration of gaseous methylenecyclobutane and 1-methyl-1-cyclobutene to 1-methylcyclobutanol in aqueous nitric acid solution have been determined by measuring the rate of drop in the saturated vapor pressure of olefin over the solution in which the reaction occurs.[2]

Demjanow and Dojarenko have shown that methylenecyclobutane is converted to 1-methylcyclobutanol by treatment with 66% H_2SO_4.[3] We find no evidence that rearranged products are formed during the hydration.

Rates and equilibria in the hydration of the small ring olefins have been investigated in order to provide critical evidence concerning the reaction mechanism. Taft has proposed that the rate-determining step in the aqueous acid-catalyzed aliphatic olefin–*t*-carbinol interconversion involves the isomerization of π-complex and carbonium ion intermediates.[4] Several criteria of mechanism indicate that the same mechanism is involved for the small ring as for the open chain olefins.[4,5]

By combining the results of the present research with those of previous investigations, we have obtained data on the effect of structure on the thermodynamic equilibrium and rate properties for the hydration of small ring olefins relative to that for corresponding open chain olefins. This information provides new evidence in support of Taft's mechanism.

Experimental

Methylenecyclobutane.—The zinc reduction of pentaerythrityl tetrabromide[6] was carried out in a manner similar to that described by Roberts and Sauer.[7] In order to separate the olefins in the crude product from spiropentane, the reaction product was extracted several times with almost saturated aqueous silver nitrate solution and the olefin was regenerated by warming the solution.[8] The crude olefin product was fractionated through a 40-inch column packed

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[1] The work reported herewith was carried out as Project NR055-295 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is 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**, 3972 (1951).

[3] I. N. Demjanow and M. Dojarenko, *J. Russ. Phys. Chem. Soc.*, **45**, 176 (1913); *Chem. Zentr.*, **84**, I, 2026 (1913); *C. A.*, **7**, 2226 (1913).

[4] (a) R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

[5] (a) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *ibid.*, **75**, 1253 (1953); (b) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

[6] *Org. Syntheses*, **31**, 82 (1951).

[7] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[8] *Cf.* M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

with glass helices. The material used for the kinetic work had a b.p. 40.8–41.0° (737 mm.), n^{20}_D 1.4206. Literature values[9] for these constants are b.p. 41.4° (750 mm.), n^{20}_D 1.4210. The infrared spectrum of the gaseous olefin sample was taken in a 10-cm. gas cell at a pressure of 5 cm. and corresponded closely to that reported by Cleveland, Murray and Galloway.[10]

1-Methyl-1-cyclobutene.—A mixture of this olefin and methylenecyclobutane was prepared following a procedure of Shand, Schomaker and Fischer.[9] Methylenecyclobutane was treated with HI and the resulting 1-methyl-1-cyclobutyl iodide was dehydrohalogenated with alcoholic KOH. The earlier workers obtained a sample containing 1-methyl-1-cyclobutene in a ratio of 2 to 1 to its exo isomer.[9] Our sample contained more nearly equivalent amounts of the two olefins (*cf.* Kinetic Procedure). The infrared spectrum of the gaseous mixture showed only the peaks reported for the two olefins.[10]

1-Methyl-1-cyclobutanol.—This carbinol was prepared in over 80% yield by the hydration of methylenecyclobutane with a 1:1 (by volume) mixture of aqueous sulfuric acid.[11] The crude product was dried over calcium hydride and fractionated through a 10-inch Vigreux column, b.p. 115–116° (uncor.) at 730 mm., n^{20}_D 1.4343. Literature values[9,16b] for these constants are b.p. 115–118° (at 747 mm.), n^{24}_D 1.4333. There was no evidence of the formation of other products such as cyclobutanemethanol (b.p. 142–143.5°, n^{20}_D 1.4450; H. Pines, H. G. Rodenberg and V. N. Ipatieff, THIS JOURNAL, **75**, 6065 (1953)) or 1-methylcyclopropane methanol (b.p. 128° at 750 mm., n^{20}_D 1.4308; S. Siegel and C. G. Bergstrom, THIS JOURNAL, **72**, 3815 (1950)—*cf.* further comment on reaction product from kinetic experiments).

Kinetic Procedure for Methylenecyclobutane.—The apparatus and the hydration procedures are those described in the study of the hydration of 1-methyl-1-cyclopentene.[12] The rate of hydration, k_p, of gaseous methylenecyclobutane at unit pressure in the gas phase by an aqueous nitric acid is given by the expression[2]

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

where

$$s = \frac{-d \ln (P - P^e)}{dt}$$

P = partial pressure of gaseous olefin at any time t

P^e = partial pressure of olefin when reaction has reached equilibrium

k_{-1} = rate of dehydration of aqueous alcohol at unit concentration (negligible in the present case)

r = ratio of volume of gas phase to volume of acid solution

h = distribution constant of olefin between liquid and gas phase

Since the distribution constant, h, was determined by separate experiments, it was possible to determine a k_p value from a single kinetic run. In general, four kinetic runs were made with values of r/RT ranging from 0.05 to 0.150 and the average k_p calculated. The probable errors given in Table III are based upon deviations from the mean.

Distribution constants in acid solutions were estimated[13] from the value obtained in water, h_0, by using the Setschenow equation

$$\log (h_0/h) = KC$$

The value of the Setschenow parameter, K, at 25.17° was obtained from the value of h_0 (Table IV) and the value of h obtained indirectly in 3 M nitric acid. Nine hydration experiments in 3 M acid at varying values of r/RT were made (results are listed in Table I). Use was then made of the relationship[2]

$$\frac{RT}{rs} = \frac{1}{k_p} + \frac{hRT}{k_p r}$$

From the least squares calculation a value of h = 22.6 ± 2.0 × 10^{-3} mole-l.$^{-1}$ atm.$^{-1}$ is obtained. Accordingly, K = −0.056 ± 0.013.

TABLE I

HYDRATION OF METHYLENECYCLOBUTANE IN 2.995 M NITRIC ACID AT 25.17°

$r/RT \times 10^3$	33.71	46.38	49.94	60.23	79.51
$s \times 10^2$	7.68	6.52	6.60	5.60	4.39
$r/RT \times 10^3$	142.0	151.7	152.2	158.9	
$s \times 10^2$	2.70	2.45	2.60	2.50	

The equilibrium pressures obtained in the hydration of methylenecyclobutane were not equal to the solvent pressures but slightly larger. This difference was independent of a variation of r/RT from 0.05 to 0.150 and independent of temperature, both of which would have a large effect if the residual pressure were due to reversibility. In all experiments this residual corresponded to about 3% of the amount of original olefin introduced. No drift was noted in the equilibrium pressures after 10 half-lives and no systematic deviation from linearity could be detected in any of the rate plots which were followed to as much as 95% of complete reaction. It was therefore concluded that 3% of an inert impurity was present in the methylenecyclobutane. It has been shown previously that the presence of a small amount of inert gas (air) does not affect the measurements when the hydration is irreversible.[2] The infrared spectrum of a gas sample enriched in this impurity was obtained by "hydrating out" methylenecyclobutane. The spectrum shows large absorption peaks at 10.07 and 12.57 μ which were barely noticeable in the original sample. The enrichment factor of both peaks was comparable. The absorption peak at 10.07 μ is identical in position and appearance with that from a spiropentane sample.[10]

Kinetic Procedure for 1-Methyl-1-cyclobutene.—The rates of hydration of gaseous 1-methyl-1-cyclobutene and methylenecyclobutane were determined simultaneously in 2.52 M nitric acid solution at 25.0°. The procedure used is that given previously,[12] and the olefin mixture used was that obtained from the dehydrohalogenation of 1-methyl-1-cyclobutyl iodide. The methylenecyclobutane reacts so much faster (about seven times) than its endo isomer that no difficulty was encountered in precisely resolving a plot (Fig. 1 is a typical example) of log P *vs.* t into the two first-

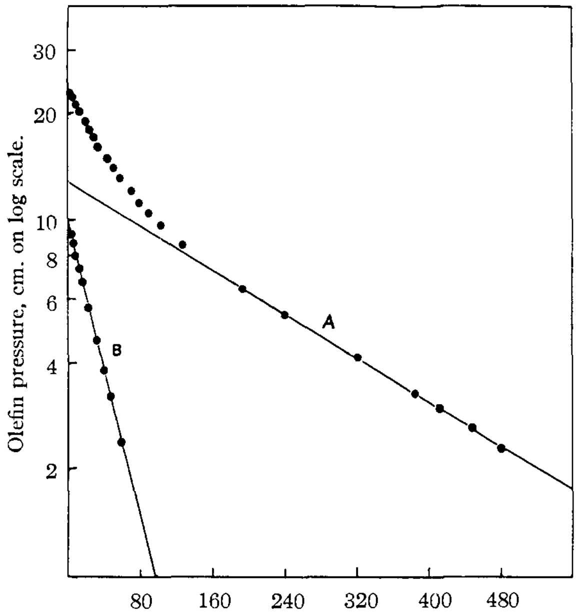

Fig. 1.—Parallel first-order hydration of 1-methyl-1-cyclobutane (A) and methylenecyclobutane (B).

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[9] W. Shand, Jr., V. Schomaker and J. R. Fischer, THIS JOURNAL, **66**, 636 (1944).

[10] F. F. Cleveland, M. J. Murray and W. S. Galloway, *J. Chem. Phys.*, **15**, 742 (1947).

[11] For details of this preparation, see P. H. Williams, Ph.D. Thesis, The Pennsylvania State College, 1941.

[12] R. W. Taft, Jr., J. Levy, D. Aaron and L. P. Hammett, THIS JOURNAL, **74**, 4735 (1952).

[13] R. W. Taft, Jr., E. L. Purlee and P. Riesz, *ibid.*, **77**, 899 (1955).

order components using conventional procedure.[14] The plot becomes precisely linear after about 75% of the original olefin has reacted, and the resulting slope, $s/2.303$, used in the equation, $k_p = (r/RT + h)(s)$, provides a value of k_p for the slower reacting olefin. Typically the k_p value is based upon the pressure drop from about 6 to 2 cm. with an initial pressure of 20 to 25 cm. The partial pressure due to the slower reacting olefin was calculated from the first-order rate law and subtracted from the observed pressure to obtain the partial pressure of the faster reacting isomer. These pressures followed precisely a first-order rate law (*cf.* Fig. 1) from which, in turn, the k_p value for the faster reacting olefin was obtained. Intercepts in the log P *vs.* t plots indicate that the composition of the olefin sample is approximately 45% in the latter olefin. Table II lists results obtained in several experiments.

TABLE II

SIMULTANEOUS HYDRATION OF 1-METHYL-1-CYCLOBUTENE AND METHYLENECYCLOBUTANE IN 2.523 *M* NITRIC ACID AT 25.0°

r/RT	k_p, 10^4 moles-l.$^{-1}$-atm.$^{-1}$-min.$^{-1}$ 1-Methyl-1-cyclobutene	Methylene-cyclobutane	Intercept ratio
0.1078	4.77	33.0	1.3
.1165	4.62	32.6	1.3
.1167[a]	4.60		4.3
.1325[b]	4.70	32.1	1.3
.1498	4.76	30.3	1.2
Mean value	4.64	32.0	

[a] Experiment with enriched 1-methyl-1-cyclobutene sample. [b] Concentration of acid 2.55 *M*.

The mean value of k_p identifies the faster reacting olefin as methylenecyclobutane. The rate of hydration of this olefin has not previously been determined in 2.52 *M* HNO_3 but has been shown to follow the equation log $k_p = (-1.29)\,H_0 - 3.53$ for the range 0.973 to 4.94 *M* HNO_3.[4b] The observed value agrees substantially with that calculated from this equation. Combined with the earlier data, the hydration rates for methylenecyclobutane are best fitted by the equation log $k_p = (-1.27)H_0 - 3.49$.

In order to check the above results, methylenecyclobutane was "hydrated out" of the original olefin sample, giving a sample which by kinetic analysis (ratio of intercepts) and by infrared analysis contained 80–85% of 1-methyl-1-cyclobutene. Hydration of this sample gave results in good agreement with those from the original sample (*cf.* Table II).

The olefin sample enriched in 1-methyl-1-cyclobutene was used to obtain a rough measure of the solubility of this olefin in 2.52 *M* HNO_3 solution at 25.0°. The procedure followed was that of Taft, Purlee and Riesz[13] (equation 1 of this reference is given incorrectly; it should read: $P^e = P + \rho(t - t')$); the value of h obtained using equation 3 of this reference is 0.010 mole-l.$^{-1}$.

Reaction Product from Kinetic Experiments.—A sample of about 1 ml. of methylenecyclobutane was allowed to react at 45° for about 10 half-life periods with 0.973 *M* nitric acid under conditions essentially identical with those prevailing during a rate measurement. The resulting solution was saturated with sodium chloride and extracted several times with carbon tetrachloride. The carbon tetrachloride solution was dried over sodium carbonate and filtered. The infrared spectrum of this solution showed the same absorption peaks as a solution of 1-methyl-1-cyclobutanol in carbon tetrachloride and no trace of any other substance could be detected. (For example, the spectrum is distinctly different from that given by V. A. Slabey and P. H. Wise, THIS JOURNAL, **71**, 3252 (1949), for α-methylcyclopropanemethanol.) The following peaks (in μ) were observed in the infrared spectrum of 1-methyl-1-cyclobutanol in carbon tetrachloride: 2.80w, 3.04w, 3.40m, 6.89m, 7.01w, 7.28m, 7.95s, 8.49m, 9.81w, 10.47s, 10.89w. Liquid 1-methyl-1-cyclobutanol gives essentially the same spectra with the following modifications: 2.80 missing, 3.04s, 8.49s, 14.00w.

Test for Deuteration or Isomerization of Methylenecyclobutane.—Gaseous methylenecyclobutane was shaken at 45° with 0.973 *M* nitric acid in 60% deuterated water under the conditions of a rate experiment until the pressure had fallen to half of the initial value. The residual olefin was then removed and its infrared absorption observed in the gaseous state with a path length of 10 cm. at a pressure of 5 cm. Comparison of this spectrum and that of the original olefin showed that no detectable deuteration or isomerization of the olefin occurs during the hydration reaction.

Dehydration of 1-Methylcyclobutanol.—The gaseous material obtained as indicated in the Results section gave the following infrared peaks (in μ) which were used to characterize isoprene (we are indebted to Professor J. D. Roberts for suggesting this assignment): 6.25m, 10.08m, 11.04s and 11.20s. Peaks at 5.96 (w), 7.00 (w) and 11.40 (s) characterize methylenecyclobutane. 1-Methyl-1-cyclobutene was identified by peaks appearing at 6.90 (m), 7.80 (w), 11.40 (s), 11.68 (s) and 3.68 (m). The quantitative analysis of the olefin mixture was based upon the following peaks: 1-methyl-1-cyclobutene, 13.68 μ; isoprene, 6.25, 10.08 and 11.04 μ; methylenecyclobutane, 5.96 and 11.40 μ. The analysis given has been rounded off to the nearest 5% and is estimated to be accurate within this limit.

Results

Rate Data.—Measurements of the rate of hydration of methylenecyclobutane in 0.972 *M* nitric acid have been made for the temperature range 25 to 45°. In this temperature range the hydration is, within the precision of measurement, completely irreversible. Table III lists the rate constants, k_p, obtained.

TABLE III

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS METHYLENECYCLOBUTANE IN 0.972 *M* NITRIC ACID IN 10^4 MOLES-L.$^{-1}$-ATM.$^{-1}$-MIN.$^{-1}$

Temp., °C.	25.17	34.58	45.15
k_p	3.97	9.47	22.75
Probable error	0.036	0.072	0.15

A plot of log k_p against $1/T$ is linear essentially within the precision of measurement. Thus the value of $10^4\,k_p$ in 0.972 *M* nitric acid at 34.58° calculated on the basis of this linearity from the value at 25.17° is 9.31 ± 0.06, compared with the observed value 9.47 ± 0.07.

From equations 8 and 9 of reference 3, we calculate the best values of the enthalpy of activation, $\Delta H_p^{\ddagger}$, to be 15.83 ± 0.11 kcal. and the entropy of activation, $\Delta S_p^{\ddagger}$, to be -28.81 ± 0.34 cal./deg. These quantities represent the difference in enthalpy and entropy between the activated state in solution on the one hand and the gaseous olefin and aqueous acid on the other.

The rate constants, k_p, obtained for 1-methyl-1-cyclobutene and methylenecyclobutene in 2.52 *M* nitric acid at 25.0° are 4.69×10^{-4} and 3.20×10^{-3} mole-l.$^{-1}$-atm.$^{-1}$-min.$^{-1}$, respectively. The value of k_p for 1-methyl-1-cyclobutene in 0.973 *M* nitric acid at 25.0° may be estimated as 6.8×10^{-5} mole-l.$^{-1}$atm.$^{-1}$-min.$^{-1}$ by the relationship: log $(k^2/k^1) = (-1.25)\,(H^2{}_0 - H^1{}_0)$.[4b]

Solubility Measurement.—The distribution constant, h, for methylenecyclobutane between gas phase and water has been measured over a temperature range from 15 to 45°. The results are recorded in Table IV.

A plot of log h against $1/T$ is linear to a reasonable precision. Thus the value of 10^3h at 34.95° calculated on the basis of this linearity from the value at 25.17° is 11.04 ± 0.08; the observed value is 10.85 ± 0.14.

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(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 149.

TABLE IV

DISTRIBUTION CONSTANT, *h*, FOR METHYLENECYCLOBUTANE BETWEEN GAS PHASE AND WATER AS A FUNCTION OF TEMPERATURE IN 10^3 MOLES-L.$^{-1}$-ATM.$^{-1}$

Temperature, °C.	16.02	19.95	25.17	30.11	34.95	45.13
h	21.56	18.99	15.49	12.63	10.85	8.01
Probable error	0.20	0.29	0.20	0.10	0.14	0.02

The heat and entropy of solution of methylenecyclobutane in water were calculated from the slope of the appropriate least squares lines. The value of the enthalpy of solution, ΔH_{sol}, is -6.43 ± 0.12 kcal. and that of the entropy of solution, ΔS_{sol} is -29.5 ± 0.4 cal./deg. The standard state is hypothetical one molal.

The rate constant for dissolved olefin at unit concentration, k_c (in units of min.$^{-1}$), is obtained from the relationship[2]: $k_c = k_{p/h}$. Using the value of h (0.010 mole-l.$^{-1}$-atm.$^{-1}$) obtained for 1-methyl-1-cyclobutene in 2.52 M nitric acid at 25.0° and the Setschenow equation with an estimated K value of 0.074,[4b] an h value for 0.973 M nitric may be estimated as 0.008 mole-l.$^{-1}$-atm.$^{-1}$. This value together with the estimated k_p value (6.8×10^{-5} mole-l.$^{-1}$-atm.$^{-1}$) gives $k_c = 9 \times 10^{-3}$ min.$^{-1}$. In a similar fashion from the data given above, the k_c value for methylenecyclobutane in 0.973 M nitric acid at 25.0° is calculated to be 2.3×10^{-2} min.$^{-1}$.

The relative enthalpies and entropies of activation, $\Delta\Delta H_c^{\ddagger}$ and $\Delta\Delta S_c^{\ddagger}$, respectively, for dissolved olefins at unit concentration (in 0.973 M HNO_3) can be obtained from the equations

$$\Delta\Delta H_c^{\ddagger} = \Delta\Delta H_p^{\ddagger} - \Delta\Delta H_{\text{sol}} \qquad (1)$$

$$\Delta\Delta S_c^{\ddagger} = \Delta\Delta S_p^{\ddagger} - \Delta\Delta S_{\text{sol}} \qquad (2)$$

The use of these equations in this manner involves the assumption that the relative enthalpies and entropies of solution, $\Delta\Delta H_{\text{sol}}$ and $\Delta\Delta S_{\text{sol}}$, respectively, are the same in one molar acid as in water. This assumption has been confirmed to a good approximation by direct measurements with isobutene and trimethylethylene.[15]

Hydration Equilibrium.—In the temperature range 25 to 45° the hydration of methylenecyclobutane was found to proceed to completion within the precision of pressure measurement. None of the olefins previously studied under comparable equilibrium conditions has been found to hydrate to this degree at 45°. It was therefore clear that the ring size of the olefin has an appreciable effect on the value of the equilibrium constant. The remarkable stability of 1-methyl-1-cyclobutanol toward dehydration has interested previous investigators.[16]

We have been able to estimate a maximum value for the equilibrium constant at 70° for the reaction

$$\text{methylenecyclobutane (g)} + H_2O(l) \rightleftarrows \text{1-methyl-1-cyclo-butanol(aq)}$$

Using a one molar (nearly saturated) solution of the carbinol in 0.0973 M perchloric acid at 70°, a steady olefin pressure of about 0.7 cm. developed with long standing. Assuming, in accord with the experimental results given below, that not more than 20% of the generated olefin is methylenecyclobutane, an equilibrium constant, $K_p = C_a^e/p_0^e$, of greater than 500 moles-l.$^{-1}$-atm. is obtained.

A solution 0.9 M in 1-methyl-1-cyclobutanol and 0.3 M in $HClO_4$ was heated at reflux temperature for several hours, during which time a stream of nitrogen was swept through the system and the exit vapors were passed into a liquid nitrogen trap. The olefin sample collected was analyzed by infrared spectra in a 10-cm. gas cell at a pressure of 4.9 cm. The analysis indicated the decomposition product to be a mixture of approximately 45% 1-methyl-1-cyclobutene, 35% isoprene and 20% methylenecyclobutane. The formation of isoprene readily is pictured in the dehydration of 1-methyl-1-cyclobutanol in terms of a Whitmore β-cleavage of a C–C bond of the cyclobutane ring.

An estimate of the relative thermodynamic stability of the endo and exo isomers may be made from the present results. Assuming the composition of the dehydration product given above to provide a rough measure of the relative rates of formation of the two olefins from aqueous carbinol solution at 25°,[17] one may calculate from this and the relative hydration rates, k_p, that the free energy of formation of gaseous 1-methyl-1-cyclobutene is on the order of 1,5000 cal./mole more negative than that for methylenecyclobutane. Turner and Garner have recently reported results indicating that in 5- and 6-membered rings the 1-methyl-1-cycloalkene is also more stable than its methylenecycloalkane isomer.[18]

Discussion

By combining the data of the present research with that of previous investigations,[19] the effects of ring size on the rates, equilibria and thermodynamic properties given in Tables V and VI are obtained. The standard of comparison is isobutylene which apparently possesses properties reasonably typical of open-chain olefins leading to *t*-carbinols. Thus, the rates of hydration relative to isobutylene are: 2-methyl-2-butene, 0.67; 2-methyl-1-butene, 1.30; 2,3,3-trimethyl-1-butene, 1.20. The rates of dehydration relative to *t*-butyl alcohol are: *t*-amyl alcohol, 10 (to give 2-methyl-2-butene) and 2.0 (to give 2-methyl-1-butene); and dimethyl-*t*-butylcarbinol, 15. These relative rates and those given in Tables V and VI apply to dissolved reactants at unit concentration in one molar nitric acid solution at 30°.

The equilibrium data of Table V indicate that the formation of carbinol from olefin is favored ($K/K_0 >> 1$) by a very substantial factor when the carbon atom forming the C–O bond is in a 4-membered ring, but the reverse ($K/K_0 << 1$) is true for the 5-membered ring. A factor of greater than four powers of ten favors the hydration equilibrium constant for methylenecyclobutane compared to

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(15) E. L. Purlee, R. W. Taft, Jr., and C. A. De Fazio, THIS JOURNAL, **77**, 837 (1955).

(16) (a) Reference 10; (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(17) If, as seems less likely, the composition of the dehydration product is equilibrium controlled, then the figure for the estimated difference in the free energy of formation of the two isomers should instead be about 500 cal./mole (favoring the endo compound). It is probable that the correct figure lies between 500 and 2000 cal./mole.

(18) R. B. Turner and R. H. Garner, THIS JOURNAL, **79**, 253 (1957).

(19) References 2, 4, 5, 12, 13, 15 and unpublished data of C. A. DeFazio.

TABLE V

EFFECT OF RING SIZE ON HYDRATION OF OLEFINS

Olefin	Reaction equilibria			Reaction rates		
	K/K_0 at 30°	$\Delta\Delta H°_c$, kcal.	$\Delta\Delta S°_c$, e.u.	k/k_0 at 30°	$\Delta\Delta H_c^{\ddagger}$, kcal.	$\Delta\Delta S_c^{\ddagger}$, e.u.
Isobutene	(1.00)	(0.0)	(0.0)	(1.00)	(0.00)	(0.00)
1-Methyl-1-cyclopentene	0.0073	3.7 ± 0.7	2.9 ± 1.6	2.29	−1.2 ± 0.6	−2.3 ± 1.4
Methylenecyclobutane	>200	....	....	0.60	1.5 ± 0.3	4.4 ± 0.8
1-Methyl-1-cyclobutene	>30	....	....	0.2	....	....

TABLE VI

EFFECT OF RING SIZE ON DEHYDRATION OF CARBINOLS

Carbinol	Reaction equilibria			Reaction rates		
	K/K_0 at 30°	$\Delta\Delta H_{-1}$, kcal.	$\Delta\Delta S_{-1}$, e.u.	k/k_0 at 30°	$\Delta\Delta H^{\ddagger}_{-1}$, kcal.	$\Delta\Delta S^{\ddagger}_{-1}$, e.u.
t-Butyl alcohol	(1.00)	(0.0)	(0.0)	(1.00)	(0.0)	(0.00)
1-Methyl-1-cyclopentanol	140	−3.7 ± 0.7	−2.9 ± 1.6	315	−4.9 ± 0.4	−5.2 ± 1.0
1-Methyl-1-cyclobutanol	<0.005[a]	....	....	<0.003[a]	....	....

[a] Based on dehydration to methylenecyclobutane.

that for 1-methyl-1-cyclopentene. The results are in accord with the I-strain hypothesis of Brown.[20] According to this hypothesis increasing the coördination number of the carbon atom of the 4-membered ring from three to four (olefin to alcohol) is favorable because of the release of some ring strain. That is, constraint of the carbon valences to 90° involves less strain in the normally tetrahedral than in the trigonal state. Further, the unfavorable effect resulting from the increase from three to four of the coördination number of the carbon atom of the 5-ring system is explained on the basis of increased eclipsing of ring hydrogen atoms.

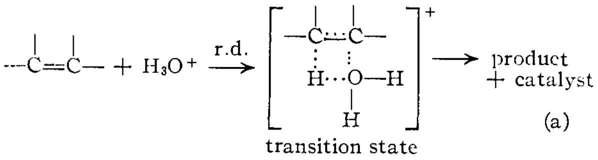
The rate of hydration (Table V) shows no such dependence on structure. In general there is relatively little effect of structure on the hydration rate. The maximum factor of one power of ten in the hydration rate involves exactly the opposite relationship to structure as that shown by the equilibria; namely, the 5-ring olefin, 1-methyl-1-cyclopentane, hydrates about ten times faster than the 4-ring olefin, 1-methyl-1-cyclobutene.

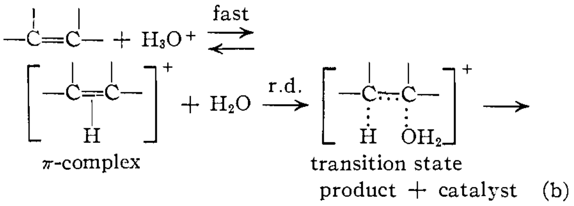
It is striking to note that in each case where temperature coefficients of rate or equilibrium have been determined (*cf.* Tables V and VI) the effects of structure on the relative free energy changes are accompanied by even larger effects in the same direction on the enthalpy changes.

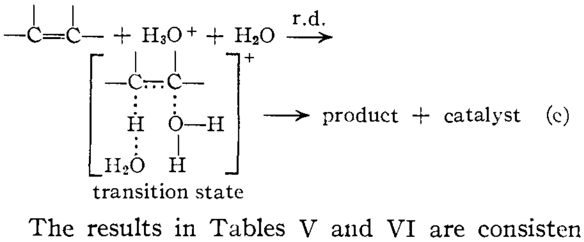
We conclude that there is no appreciable covalent bonding of a water molecule to carbon in the hydration transition state. The argument is based upon the proposition that if the transition state resembled the carbinol (with appreciable covalent C–O bond interaction), the effect of structure on the hydration rate and on the equilibrium would be in the same direction and of similar magnitude. That is, similar effects from increasing the coördination number of the ring carbon atom would result from the formation of either the transition state or the carbinol from the olefin. The relationships expected on this basis are not observed.

On the other hand, the formation of both the transition state and the olefin from the carbinol are similarly affected (in direction and in magnitude) by structure (compare corresponding values of K/K_0 and k/k_0 of Table VI). The direction of the observed effects are those expected according to the I-strain hypothesis for the decrease in coördination number of the ring carbon atom from four (carbinol) to three (olefin or transition state). In other words, the closely similar effects of structure on the rate and equilibrium of carbinol dehydration indicate that the water present in the conjugate acid of the carbinol is lost from carbon in the formation of either the olefin or the transition state. A similar conclusion has been reached earlier based upon the entropies of activation and reaction for olefin hydration and carbinol dehydration.[4]

The present results, therefore, exclude such mechanisms as the following (as well as those rigorously excluded by earlier results[5])







The results in Tables V and VI are consistent with, and lend further support to, the mechanism of Taft (given below) which pictures no appreciable covalent interaction between oxygen (of H_2O) and carbon (of olefin) in the proposed transition state.

Apparently the only alternate mechanism which is consistent with the present results is a rate-determining proton transfer from hydronium ion to olefin. This mechanism is considered to be of low probability on the basis of observed isotope effects on the hydration rate.[5b]

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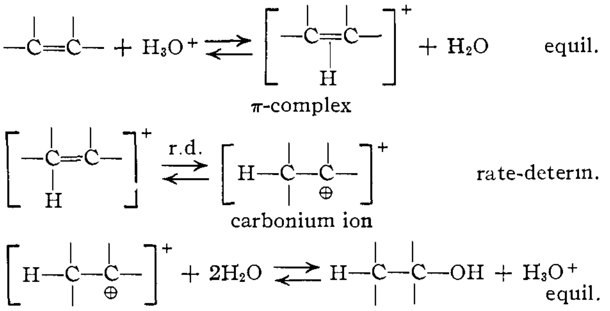
[20] (a) Reference 17b; (b) H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951); (c) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).



$$-\overset{|}{C}=\overset{|}{C}- + H_3O^+ \rightleftarrows \left[\underset{H}{-\overset{|}{C}=\overset{|}{C}-}\right]^+ + H_2O \qquad \text{equil.}$$

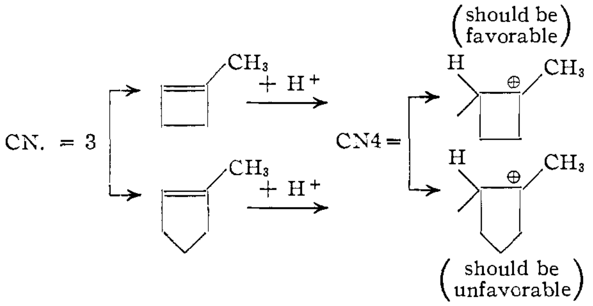
π-complex

$$\left[\underset{H}{-\overset{|}{C}=\overset{|}{C}-}\right]^+ \overset{\text{r.d.}}{\rightleftarrows} \left[H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\oplus}{C}}-\right]^+ \qquad \text{rate-determ.}$$

carbonium ion

$$\left[H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\oplus}{C}}-\right]^+ + 2H_2O \rightleftarrows H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH + H_3O^+ \qquad \text{equil.}$$

Application of the I-strain hypothesis to the relative rates of olefin hydration listed in Table V provides further evidence of importance concerning the structure of the transition state. If the positions occupied by the nuclei in the reaction transition state were those expected of a classical carbonium ion (in which the added H has formed a conventional C–H bond), then by arguments paralleling those used above, the rate of hydration of the cyclobutene should be favored and the cyclopentene retarded relative to the open chain olefins



However, as noted above, exactly the opposite order of rates is observed. We conclude therefore that the transition state does not possess the nuclear arrangement of a classical carbonium ion. On the other hand, the transition state is stabilized by those structural features which by electronic shifts (inductive or hyperconjugative electron-release) stabilize carbonium ions, as witnessed by the many powers of ten increase in rate in the series: ethylene << propylene << isobutylene.[21] The olefin hydration transition state may thus be ascribed the property of possessing carbonium ion character with respect to electronic but not with respect to molecular structure (nuclear arrangement). This property bears a striking similarity to the well-known Franck–Condon principle and, by analogy, leads to the proposal that the property results from more sluggish nuclear than electronic rearrangements in attaining the transition state.

It is a corollary of our conclusions that the transition state cannot be said (as frequently implied in discussions) to possess a fixed fractional character of the products and reactants of the rate-determining step, but this assessment, if it is to be generally useful, must be made with respect to both electronic and nuclear rearrangements.

Since the effects of structure on hydration rates shown in Table V are relatively small (compared to the effects on dehydration rates shown in Table VI), the π-complex appears to provide a suitable model for the molecular structure of the transition state. According to the structure proposed from the π-complex,[22] its formation from olefin should not require notable nuclear rearrangements.

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(21) This is in contrast to the formation constants of the Ag^+ complexes of these olefins which show relatively little dependence on structure; *cf.* F. R. Hepner, K. N. Trueblood and H. J. Lucas, THIS JOURNAL, **74**, 1333 (1952).

(22) (a) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); (b) C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 46; (c) E. L. Purlee and R. W. Taft, Jr., THIS JOURNAL, **78**, 5807 (1956); (d) L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956).

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Dialysis Studies. II. Some Experiments Dealing with the Problem of Selectivity

BY LYMAN C. CRAIG, TE PIAO KING AND ALFRED STRACHER[1]

RECEIVED FEBRUARY 6, 1957

A convenient cellophane dialysis cell for quantitatively studying dialysis rates is described. A series of proteins of increasing molecular weight up to 45,000 have been studied. The rate of dialysis for each protein has been shown to fall in the order of increasing molecular weight but the membrane becomes more selective as the solute size approaches the membrane pore size. The method may offer a simple means for detecting a change in shape or size during certain types of transformation and for studying homogeneity with respect to size.

In the first paper[2] of this series an experimental approach for fractional dialysis with cellophane was described which permitted multiple fractional separations to be made in a manner entirely analogous to that accomplished with a few stages of countercurrent distribution.[3] Evidence of unanticipated selectivity was encountered at that time which was sufficient to make the procedure as it was described of practical use for the preliminary fractionation of complex mixtures of solutes differing widely in size. It seemed likely that the overall selectivity of the method could be improved either by enhancing the inherent selectivity at each stage or by some mechanical systematization so that many stages could be applied with a minimum of labor as was done in countercurrent distribution.

This latter is made difficult by the fact that for each unit in a stage the dilute dialyzate must be concentrated in some way to one tenth or less of its volume before being transferred to the inside of the next unit in the series. Before attempting to

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(1) Fellow of the National Foundation for Infantile Paralysis.

(2) L. C. Craig and T. P. King, THIS JOURNAL, **77**, 6620 (1955).

(3) L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944).