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

Distribution Constants for Ethylene and Propylene between the Gas Phase and Aqueous Perchloric Acid[1]

BY E. LEE PURLEE[2] AND ROBERT W. TAFT, JR.

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The solubilities of ethylene and propylene in 0–60% aqueous perchloric acid at 30° are reported. An estimate for the minimum energy of π-complex formation is obtained. The observed "salt effects" on olefin solubility are discussed.

Introduction

In an earlier paper kinetic evidence has been presented indicating the existence of a π-complex preceding the rate-determining step in the acid-catalyzed hydration of ordinary aliphatic olefins leading to *t*-alcohols.[3] The solubilities of such olefins in acid solutions up to approximately four molar, however, show no evidence of a measurable conversion to the π-complex. Usual "salting in" or "salting out" behavior is exhibited.[4]

In the present work we have determined the solubilities of the much less reactive olefins, propylene and ethylene, in concentrated perchloric acid solutions at 30.00°. The results provide further evidence that the π-complex, if it exists, must be a very unstable reaction intermediate in olefin hydration.

Experimental

The apparatus and methods employed were those previously described.[4] Temperature was maintained at 30.00 ± 0.01°.

Ethylene (99.5%) and propylene (99.7%) were obtained from the Matheson Company. Perchloric acid was Baker C.P. grade.

Results

The distribution constants, *h*, between the vapor phase and the aqueous solutions are listed in Table I. Each value reported is the average of ten to fourteen determinations.

TABLE I

DISTRIBUTION CONSTANTS, *h*, FOR ETHYLENE AND PROPYLENE BETWEEN THE VAPOR PHASE AND AQUEOUS PERCHLORIC ACID SOLUTIONS AT 30.00° IN UNITS OF 10^3 MOLES-L.$^{-1}$-ATM.$^{-1 a}$

$HClO_4$, wt. %	Concn., *M*	*h*, ethylene	*h*, propylene
0.00	0.00	4.11 ± 0.06	4.36 ± 0.04
9.75	1.027	3.97 ± .06	4.28 ± .04
20.80	2.34	3.74 ± .04	4.48 ± .04
32.01	3.90	3.79 ± .03	4.40 ± .06
43.60	5.85	3.24 ± .03	4.01 ± .04
53.73	7.80	2.54 ± .03	3.11 ± .04
60.71	9.36	2.10 ± .03	

[a] Uncertainties are given in terms of standard error.

No measurable rate of reaction was detected for ethylene at acidities up to and including 9.36 *M*. In 11.7 *M* (70.4%) perchloric acid solution, however, the rate of reaction of ethylene was too fast to permit solubility measurements. In the case of propylene, no measurable rate of reaction was detected at acidities up to and including 5.85 *M* solutions. In 7.80 *M* solution the hydration rate of propylene was quite perceptible, but solubility data were obtained by the technique described earlier.[4] In 9.36 *M* solution the hydration rate of propylene was too fast to permit solubility measurement.

In the concentration range 0–2.5 *M* the solubility of propylene is nearly constant (perhaps slightly "salted in"). Ethylene is "salted out" in this range. Both olefins show virtually no change in solubility in the region 2.5–4.5 *M*. Near 4.5 *M*, however, the solubilities of both olefins are characterized by an abrupt and marked "salting out" with increasing acid concentration. A Setschenow-like equation is followed with precision in both the dilute and concentrated acid regions, but different parameters are required. In Table II the Setschenow-like parameters, $K = \log(h^*/h)/c$, are reported along with their ranges of applicability. For the range 5–10 *M* acid, h^* is the solubility in about 5 *M* acid. For the 0–2.5 *M* range, *K* is the usual Setschenow parameter since h^* in this case refers to the solubility in pure water.

The precise linear relationship between log *h* and acid concentration observed in the 5–10 *M* region is of interest, especially if it represents a general behavior of the inert non-electrolytes in concentrated electrolyte solutions.

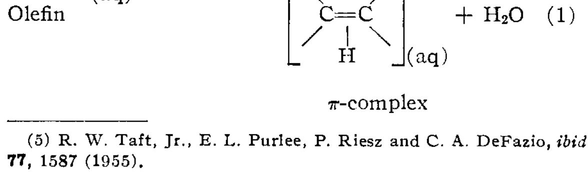
TABLE II

SETSCHENOW-LIKE PARAMETERS FOR ETHYLENE AND PROPYLENE IN AQUEOUS PERCHLORIC ACID AT 30.00°

Concn. range, *M*	Ethylene	Propylene
0–2.5	+0.0176 ± 0.0004	−0.0055 ± 0.0015
5–10	+0.054 ± 0.0005	+0.057 ± 0.006

Discussion

The "salting out" behavior exhibited by both ethylene and propylene in concentrated perchloric acid solutions provides no evidence of a measurable conversion of these olefins to π-complex. The equilibrium constant, *K*, for reaction 1 is expected



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(1) The work reported herein was carried out on Project NR 055-295 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part is permitted for purposes of the United States Government.

(2) Combat Operations Research Group, Fort Monroe, Virginia.

(3) *Cf.* E. L. Purlee and R. W. Taft, Jr., THIS JOURNAL, **78**, 5807 (1956) and earlier references given therein.

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

(5) R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, *ibid.*, **77**, 1587 (1955).

to follow the Hammett acidity function, h_0,[5] as indicated by the equations

$$K = \frac{a_\pi}{a_o a_{H^+}} = \left(\frac{c_\pi}{c_o}\right)\left(\frac{\gamma_\pi}{\gamma_o}\right)\left(\frac{\gamma_B}{\gamma_{HB^+}}\right)\left(\frac{1}{h_o}\right) = \left(\frac{c_\pi}{c_o}\right)\left(\frac{1}{h_o}\right)$$

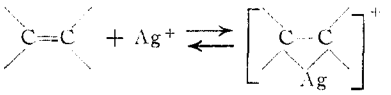
and

$$\Delta F^\circ = -2.303RT\,[\log\,(c_\pi/c_o) + H_o]$$

where a's refer to activities, c to concentrations, and γ to activity coefficients. The subscripts π and o refer to π-complex and olefin, respectively.

The fact that no measurable conversion of olefin to π-complex is detected by the solubility measurements over the range of acidities studied indicates that (c_π/c_o) probably can be no greater than 10^{-2} in 65% $HClO_4$. From this and the H_o value of about -6 for 65% $HClO_4$, one obtains the estimate that ΔF° for reaction 1 must exceed 11 kcal. This figure may also be used as an estimate for the minimum enthalpy change for reaction 1, since ΔS° for reaction 1 is expected to be near zero.[5]

Hepner, Trueblood and Lucas[6] have found rather small structural effects on the formation constants for the silver ion complexes of ordinary aliphatic olefins



By analogy, it seems likely that the estimate of a minimum figure of 11 kcal. obtained for ethylene and propylene for the ΔH^0 of reaction 1 applies as well to the more reactive olefins such as isobutylene. The activation energy for the hydration of isobutylene in one molar acid is about 22 kcal.[7] Therefore, the activation energy for conversion of the π-complex of isobutylene to t-butyl alcohol may be crudely estimated to be less than 11 kcal.

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[6] F. R. Hepner, K. N. Trueblood and H. J. Lucas, THIS JOURNAL, **74**, 1333 (1952).

[7] *Cf.* E. L. Purlee, R. W. Taft, Jr., and A. DeFazio, THIS JOURNAL, **77**, 837 (1955), and references cited therein.

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

The Reaction of Isobutylamine with Nitrous Acid. π-Complex and the Bridged-Protonium Ion[1a]

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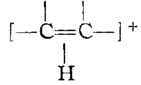
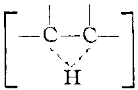
The reaction of isobutylamine and nitrous acid in aqueous solution has been carried out under controlled conditions of acidity and temperature. Seven products have been identified: t-butyl alcohol, *sec*-butyl alcohol, isobutyl alcohol, isobutylene, 1-butene, *trans*-2-butene and *cis*-2-butene. No detectable exchange of hydrogen is found in the hydrogen migration to give t-butyl alcohol when the reaction is carried out in D_2O, showing that the t-butyl cation intermediate does not undergo direct H–D exchange. Further, in view of Purlee and Taft's kinetic data on olefin hydration, the present results exclude the π-complex (of Taft's olefin hydration mechanism) as an intermediate in the hydrogen migration reaction. The present results are interpreted on the basis that the structures represented by I and II are distinct and different entities:  $[-\overset{|}{C}=\underset{\underset{H}{|}}{\overset{|}{C}}-]^+$ π-complex (I) and  $\left[-\overset{|}{C}-\overset{|}{C}-\right]^+$ (bridged by H) bridged protonium ion (II). The activation energy for hydrogen migration is about 2.5 kcal. lower than that for methyl migration, but the entropy of activation favors the latter by about 5 cal./deg.

The reactions between aliphatic amines and nitrous acid give extensive rearrangements. Whitmore and co-workers[2] accounted for the variety of products obtained from the diazotization of ethylamine, n-propylamine and n-butylamine, on the basis of a carbonium ion intermediate. Roberts and Yancey[3] found that ethylamine-1-C^{14} gives ethylene and ethanol, the latter containing 1.5% of the rearranged product, ethanol-2-C^{14}. This result indicates that the ethyl cation formed by the decomposition of the diazonium ion cannot be a bridged ethyleneprotonium ion since such an ion would give equal amounts of the two labeled alcohols. Roberts and Halmann[4] also applied the use of tracers to the study of the rearrangement of 1-propylamine-1-C^{14} and found that of the 1-propanol produced in the reaction, 8.5% had rearranged. The above authors have concluded that the reaction of aliphatic amines and nitrous acid provides as "free" a carbonium ion in aqueous solution as any known reaction.[3-5]

Evidence indicating that relatively free isobutyl, *sec*-butyl, and t-butyl cations are formed in the isobutylamine–nitrous acid reaction has been presented.[6]

The study reported in this paper was made for the purpose of finding whether a distinction must be made between the π-complex (obtained as an intermediate proceeding the rate-determining step in the hydration of ordinary branched aliphatic ole-

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[1] (a) The work reported herein was supported in part by Project NR055-295 between the Office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part permitted for any purpose of the United States Government; (b) Union Carbide and Carbon Corp. Fellow for 1954–1955; (c) taken in part from the Ph.D. Thesis of Lawrence G. Cannell, The Pennsylvania State University, Jan., 1956.

[2] F. C. Whitmore and D. P. Langlois, THIS JOURNAL, **54**, 3441 (1932); F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

[3] J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952).

[4] J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953).

[5] A. W. Fort and J. D. Roberts, *ibid.*, **78**, 587 (1956).

[6] L. G. Cannell and R. W. Taft, Jr., Abstracts of Papers presented at American Chemical Society Meeting, Dallas, Texas, April, 1956, p. 46N.