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Specific Solvation in Binary Solvent Mixtures. Part II. The Dependence of Activation Energy of Solvolysis of Benzyl Chloride in Ethanol–Water Mixtures on Temperature and Ring Substitution

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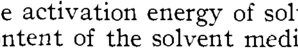
Rate constants for the solvolysis of p-H, p-CH_3, p-Cl and p-NO_2 benzyl chlorides in ethanol–water solvent mixtures are reported as a function of both solvent composition and temperature. The variation with temperature of the activation energy dependence on solvent composition is discussed in detail for the parent benzyl chloride and the effect of *para* substitution is compared in all cases. The observations provide further support for the specific solvation model presented previously.

Introduction

In the previous paper of this series[1] the frequently observed maximum or minimum through which solvolytic activation energies pass as binary solvent mixture composition is varied was interpreted in terms of differences in specificity of solvation of initial or transition states by one or the other component of the binary solvent system. The appearance of maxima or minima in such plots was shown to be dependent upon whether charge density at the reacting center is diminished or enhanced in passing from the initial to transition state configuration. The degree to which the particular state can specifically select its solvation shell components would be expected to be temperature dependent and this should be reflected in the maximum or minimum observed in the activation energy behavior at different temperatures.

As a test of this prediction we report here the detailed study of the behavior of the activation energy as a function of solvent composition at various temperatures for the solvolysis of benzyl chloride in water-rich ethanol–water mixtures. The choice of benzyl chloride as the reacting solute was dictated by several factors: (a) the rate of solvolysis of this compound is conveniently measurable over the range 25° to 80°; (b) the activation energy minimum observed is sufficiently large to permit observation of changes in magnitude bearing in mind the limitations of accuracy with which activation energies can be measured; and (c) to permit the study of the dependence of activation energy behavior on ring substitution.

It is generally accepted[2] that the solvolysis of benzyl chloride proceeds by an essentially SN1 mechanism with development of charge in the activation process, *i.e.*, where R = $C_6H_5CH_2$–



$$\underset{\text{initial state}}{\text{R–X}} \longrightarrow \underset{\text{transition state}}{\overset{\delta_+}{\text{R}}\text{---}\overset{\delta_-}{\text{X}}} \longrightarrow$$

It was previously argued[1] that the minimum observed in the activation energy of solvolysis as the ethanolic content of the solvent medium increased resulted from a higher degree of specific solvation of the ion-like transition state by the more polar water compared with the initial state. It was further shown that the greater the extent of charge creation attained in the transition state the greater would be the difference in specificity of solvation between initial and transition state. This, in turn, would lead to an increase in the depth of the minimum, $\Delta\Delta E^*$, defined as the difference between the activation energy in water and the value at the minimum. It was observed that as the alkyl group R is varied through a series of structures with increasing ability to carry positive charge the depth of the observed minimum increased. In one series of alkyl groups the order of increasing depth of minimum was $CH_3 < C_2H_5 < n\text{-}C_3H_7 < i\text{-}C_3H_7 < C_6H_5CH_2 < t\text{-}C_4H_9 < CH_3(C_6H_5)CH$. It was noted that this is precisely the order of increasing stability of the corresponding carbonium ions.

In order to test this hypothesis further, the solvation activation energies for a series of p-substituted benzyl chlorides were determined as a function of water–ethanol solvent composition. The ring substituents chosen were p-methyl, p-hydrogen, p-chloro and p-nitro, representing a range of inductive effects from electron donating to strong electron withdrawing. The p-methyl substituent should promote ion creation in the transition state by stabilizing the incipient carbonium ion. The specific solvation model predicts that this effect should be reflected in an enhancement of the extremum behavior of the activation energy compared with the unsubstituted benzyl chloride. Conversely the electron-withdrawing substituents should cause a diminution in the extremum behavior compared with benzyl chloride.

Experimental

All first-order rate determinations for the solvolysis of the benzyl chloride systems were made by the conventional conductometric method[3] using an a.c. bridge at 1000 c.p.s. Temperature control was by oil thermostating to better than ±0.01°. The observed resistance *versus* time data were analyzed by the Guggenheim method[4] and gave excellent straight line plots. At the concentrations of solute employed the concentration of HCl produced is an excellent linear function of conductance in all solvent compositions employed.

Solvent systems were prepared by weight from double distilled water (conductance 1×10^{-7} mho) and redistilled absolute ethanol (n^{25}D 1.3593). All benzyl chlorides were repurified before being used in the preparation of 10^{-3} *M* working solutions in the various ethanol–water mixtures. p-Chlorobenzyl chloride was twice recrystallized from dry ether yielding colorless needles, m.p. 28–29°. Similar recrystallization of p-nitrobenzyl chloride gave pale yellow platelets, m.p. 71–72°. p-Methylbenzyl chloride was redistilled at 108–112° at 20 mm., n^{20}D 1.5316. The redistilled parent benzyl chloride used had a refractive index n^{16}D 1.5417, in excellent agreement with the literature value.

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[1] J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960).

[2] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, N. Y., 1959, p. 256.

[3] R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955).

[4] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

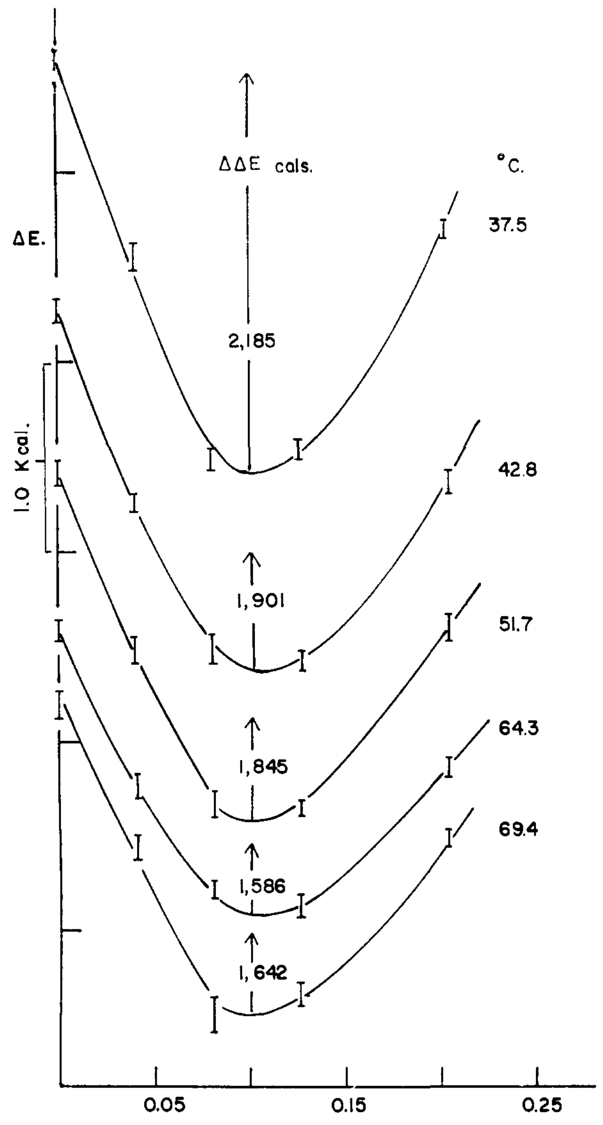

Fig. 1.—Activation energy *versus* solvent composition for solvolysis of benzyl chloride at various temperatures.

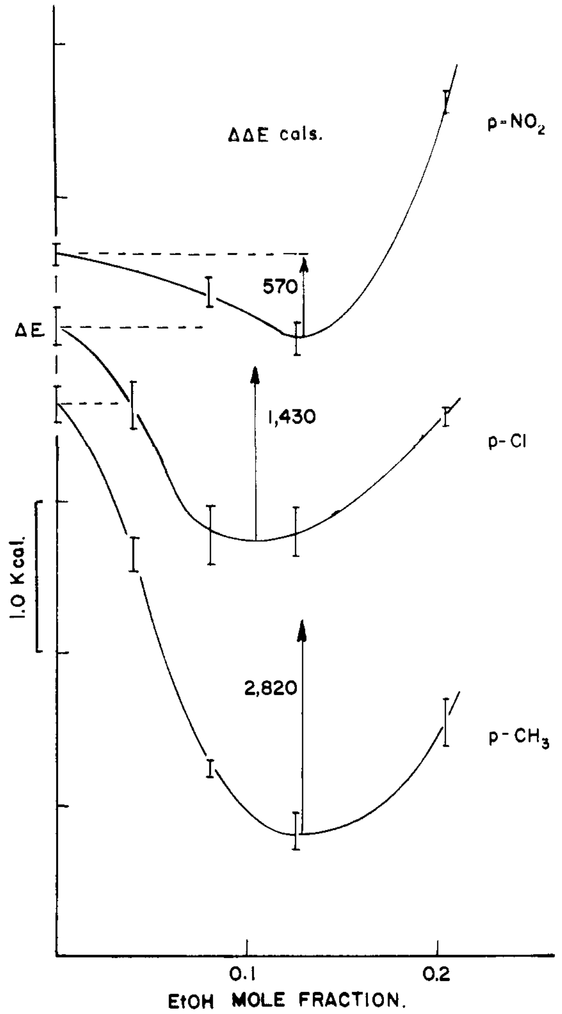

Fig. 2.—Activation energy *versus* solvent composition for solvolysis of *p*-substituted benzyl chlorides in ethanol–water mixtures.

Results

First-order rate constants for the solvolysis of the parent benzyl chloride in various ethanol–water mixtures are recorded in Table I for four temperatures in the range 25 to 80°. Since the temperature dependence of the activation energy was required in this system, maximum precision in rate values was needed. Throughout Table I an uncertainty of ±0.2% in the rate values is assumed unless otherwise stated. In Table II first-order rates for the solvolysis of the substituted benzyl chlorides are shown for the same solvent compositions but at two temperatures only. Since no temperature dependence study of activation energy was attempted in these systems, fewer replicate rate measurements were made and rate values have uncertainty limits of ±0.5%.

By taking pairs of rate constant values for a given solvent at different temperatures activation energies and entropies may be computed by the Arrhenius equation for temperatures which are the medians of the temperatures at which the rates were measured. Since it is well known that such solvolytic activation energies are temperature dependent,[5] there is no merit in using more than two rates to compute the activation energy at the median temperature since the plot of log *k* against $1/T$ would not be linear in any case. The limits of accuracy of the activation energies thus computed were determined by evaluating the activation energy using the maximum and minimum differences between the rates at the two temperatures as indicated by the limits of uncertainty of the individual rate values. The uncertainties in the activation energies are indicated on the plots in Figs. 1 and 2. As a comparison, our value for the solvolysis of benzyl chloride in pure water, $\Delta E^*_{51.65} = 21{,}005 \pm 50$ cal./mole, is in excellent agreement with that of Robertson and co-workers[6] who report $\Delta H^*_{50} = \Delta E^*_{50} - RT = 20{,}388$ cal./mole, or $\Delta E^* = 21{,}028$ cal./mole.

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[5] R. E. Robertson, *Suomen Kemi.*, **A33**, 63 (1960).

[6] R. E. Robertson, R. L. Heppolette and J. M. Scott, *Can. J. Chem.*, **37**, 803 (1959).

TABLE I

RATES AND ACTIVATION ENERGIES OF SOLVOLYSIS OF BENZYL CHLORIDE IN ETHANOL–WATER MIXTURES

Rates[a] and activation parameters	Mole fraction ethanol 0.000	0.040	0.080	0.125	0.203
$k \times 10^6$ sec.$^{-1}$ (25.00°)	13.18	9.906	6.954	3.677	1.226
$k \times 10^5$ sec.$^{-1}$ (50.30°)	22.78	14.96	9.113	4.852	1.885 (±0.4%)
$k \times 10^5$ sec.$^{-1}$ (60.50°)	60.00	37.70	23.01	11.99	4.762 (±0.3%)
$k \times 10^4$ sec.$^{-1}$ (78.30°)	28.51 (±0.4%)	16.93	9.628	5.075	2.159
ΔE^*, cal. (37.65°)	21,585	20,563	19,489	19,542	20,699
ΔE^*, cal. (42.75°)	21,261	20,264	19,485	19,403	20,377
ΔE^*, cal. (51.65°)	21,005	20,084	19,262	19,249	20,201
ΔE^*, cal. (64.30°)	20,386 (±60)	19,574	19,020	18,939	19,671 (±60)
ΔE^*, cal. (69.40°)	20,402 (±75)	19,662	18,737	18.888	19,787 (±60)

[a] All rate uncertainties ±0.2% or less and activation energies ±50 cal. unless otherwise indicated; last figure in all rates guard figure only.

TABLE II

RATES, ACTIVATION ENERGIES AND ENTROPIES OF SOLVOLYSIS OF *p*-SUBSTITUTED BENZYL CHLORIDES IN ETHANOL–WATER MIXTURES

Rates and activation parameters	Mole fraction ethanol 0.00	0.04	0.08	0.125	0.203
			p-Methylbenzyl chloride		
$k \times 10^5$ sec.$^{-1}$ (41.06°)	308.4[a]	168.7	81.80	31.25	7.503
$k \times 10^6$ sec.$^{-1}$ (22.44°)	313.5	189.0	106.5	43.96	9.174
ΔE^*, cal./mole (31.75°)	22,659	21,700	20,209	19,440	20,830
ΔS^*, e.u./mole[b]	0.0	−4.2	−10.4	−14.7	−13.1
			p-Chlorobenzyl chloride		
$k \times 10^5$ sec.$^{-1}$ (60.44°)	33.53	21.09	11.94	6.206	2.541
$k \times 10^6$ sec.$^{-1}$ (42.86°)	56.90	37.34	22.70	11.77	4.531
ΔE^*, cal./mole (51.65°)	21,137	20,627	19,780	19,810	20,545
ΔS^*. e.u./mole	−13.2	−15.7	−19.3	−20.6	−20.1
			p-Nitrobenzyl chloride		
$k \times 10^6$ sec.$^{-1}$ (78.30°)	83.70		37.77	24.39	15.44
$k \times 10^6$ sec.$^{-1}$ (60.44°)	16.06		7.373	4.882	2.735
ΔE^*, cal./mole (69.40°)	21,611		21,385	21,058	22,658
ΔS^*, e.u./mole	−17.9		−20.2	−22.0	−18.3

[a] Last figure in all rates guard figure only. [b] ΔS^* values are mean of values calculated using median temperature activation energy with rate value at each temperature; deviation approximately ±0.1 e.u.

Discussion

Temperature Dependence of $\Delta\Delta E^*$ and ΔE^* for Benzyl Chloride.—Using the same model as presented previously[1] the energies of the initial and transition states at two temperatures may be depicted schematically as shown in Fig. 3. It was proposed in the model that the initial independence of the energy of each state on the solvent composition was due to the fact that the polarity of the state dictated a high degree of specific solvation by the more polar component of the solvent, in this case water. Consequently, as the non-aqueous component is increased there will be an initial range of composition over which the solute is hydrated and the ethanol is excluded. Since the composition of the kinetically important microscopic solvation sphere does not change, the energy likewise remains constant. The range of this specificity is correspondingly greater for the more polar or ion-like transition state compared with the dipolar initial state.

As the temperature is raised, however, the additional thermal energy in the system will render it increasingly difficult for the solute, in both the initial and transition states, to maintain the specificity of solvation as the mole fraction of non-aqueous component is increased. As a consequence, the solvent independent ranges of the energies of both states will be diminished and the difference between the activation energies in water and at the minimum will decrease, *i.e.*, $\Delta\Delta E^*$ should decrease with increasing temperature as shown in Fig. 3. The experimental data of Fig. 1 clearly bear out this prediction. The depth of the minimum, $\Delta\Delta E^*$, decreases from 2.2 kcal./mole at 37° to 1.6 kcal./mole at 65°, a decrease over some 30° that is well outside the limits of uncertainty of the activation energy data. The data would suggest that the decrease is not a linear function of the temperature but this is not unexpected in view of the complexity of factors which must play an important role in determining the effect of temperature on the solvent shell structure. Furthermore, as the temperature increases, the effect of thermal energy on the specific character of the solvent shell would be expected to decrease as the amount of specific solvation itself diminishes.

Although the $\Delta\Delta E^*$ values can be determined with some accuracy from ΔE^* values of the precision quoted here, estimation of the position of the minimum on the solvent composition axis is a much more difficult problem. It is doubtful whether such estimates could be made to better than ±0.02 mole fraction in the system under

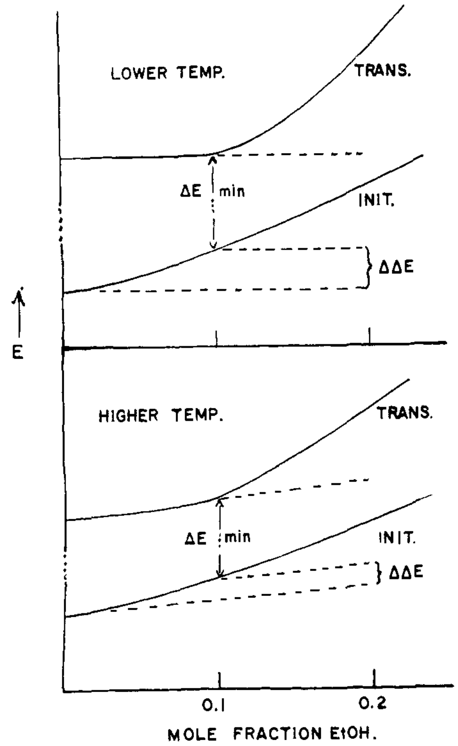

Fig. 3.—Schematic representation of activation energy behavior as a function of solvent composition and temperature based on specific solvation model.

study even with a much closer scanning of the range of points near the minimum. Within the limit of precision of the present data as plotted in Fig. 1, the position of the minimum on the solvent axis appears to be temperature independent. This is in agreement with the model as presented schematically in Fig. 3, although it is clear that the model could be modified readily to permit variation of the position of the minimum with temperature.

The activation energy data presented in Fig. 1 may also be used to compute the temperature dependence of the activation energy in each solvent composition. Although the rate data are insufficient to perform the more precise type of analysis for ΔC^*_p,[7,8] plots of ΔE^* *versus* temperature for each solvent composition of the form shown in Fig. 4 permit estimation of $\mathrm{d}\Delta E^*/\mathrm{d}T$. All values obtained are negative as has been generally found for solvolytic reactions involving creation of charge in passing to the transition state.[5,8] The value estimated for benzyl chloride in pure aqueous medium, −43 cal./°mole, is in the same range as the ΔC^*_p values for the solvolysis of methyl halides in water.[9] The trend toward less negative values of $\mathrm{d}\Delta E^*/\mathrm{d}T$ as the ethanolic content of the solvent is increased is in agreement with the observed ΔC^*_p values for the solvolysis of methyl *p*-nitrobenzenesulfonate[10] in water (~ −27 cal./°mole) and ethanol (−21 cal./°mole). It would appear from these estimates of $\mathrm{d}\Delta E^*/\mathrm{d}T$, however, that

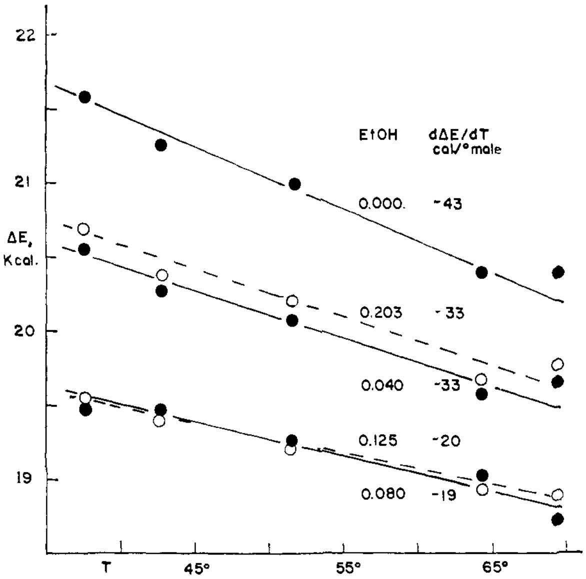

Fig. 4.—Temperature dependence of activation energy for solvolysis of benzyl chloride in various ethanol–water solvent mixtures.

this parameter of the activation process also passes through a minimum negative value in water-rich solvent mixtures. The present state of knowledge of the factors influencing the temperature dependence of the activation energy[5,7,8,10] is insufficient to warrant further interpretation of the estimates of $\mathrm{d}\Delta E^*/\mathrm{d}T$ presented here. There can be little doubt, however, that such a temperature dependence does exist and that it will provide a further tool for the investigation of solvent effects in kinetics. The activation entropy data available from the rates in Table I will be considered in a subsequent paper in this series dealing with the general problem of variations in activation entropies of solvolytic reactions in mixed solvents.

Correlation of $\Delta\Delta E^*$ with Substituent Constant σ^+.—The activation energy *versus* solvent composition plots in Fig. 2 substantiate the qualitative prediction of increasing depth of minimum as the *p*-substituent is varied through a series of groups of increasing electron-donating power. (The activation energy scale in Fig. 2 is an arbitrary one for the sake of clarity.) It was shown in the previous section of this discussion, however, that the depth of the activation energy minimum is a function of temperature. The considerable difference in the rates of solvolysis of the three benzyl chlorides at any given temperature made it more convenient to measure the rates over different temperatures ranges with the consequence that the activation energies obtained are associated with different median temperatures. In order to remove the temperature dependence factor from any quantitative comparison of the depths of minima, the corresponding value for the depth of minimum for benzyl chloride at each median temperature required was obtained from a plot of $\Delta\Delta E^*$ *versus* temperature for this system. The $\Delta\Delta E^*$ value for each substituted benzyl halide could then

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(7) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **33**, 1544 (1955).

(8) R. E. Robertson, *ibid.*, **35**, 613 (1957).

(9) R. L. Heppolette and R. E. Robertson, *Proc. Roy. Soc. (London)*, **A252**, 273 (1959).

(10) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **35**, 623 (1957).

be expressed as a fraction of the unsubstituted benzyl chloride value *at the same temperature.* The $\Delta\Delta E^*$ values for the substituted benzyl chlorides, the corresponding $\Delta\Delta E^*$ values for the unsubstituted benzyl chloride and the resultant ratios of the two values are shown in Table III.

TABLE III

$\Delta\Delta E^*$ AND σ^+-VALUES FOR *p*-SUBSTITUTED BENZYL CHLORIDES

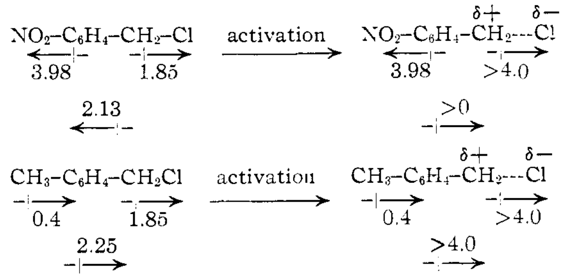
p-X	CH_3	H	Cl	NO_2
T, °C.	31.75		51.65	69.40
$\Delta\Delta E^*_{p\text{-H}}$, cal./mole	2820		1430	570
$\Delta\Delta E^*_{p\text{-H}}$, cal./mole	2240		1845	1570
$\Delta\Delta E^*_{p\text{-X}}/\Delta\Delta E^*_{p\text{-H}}$	1.26	1.00	0.78	0.36
σ^+	−0.31	0.00	+0.11	+0.79

As a relative measure of the effect of the various substituents in enhancing charge development in the transition state and so favoring specificity of solvation, we have shown the σ^+-values of Brown and Okamoto.[11] These substituent constants are based on the solvolysis of cumyl chlorides and are therefore more appropriate to the analogous solvolysis of benzyl chlorides than the more commonly used Hammett σ-values.

Comparison of the $\Delta\Delta E^*$ ratio values with the σ^+-values for each substituent as shown in Table III illustrates the obvious relationship between the two parameters. A plot of the two functions gives a shallow smooth curve, but the lack of linearity is not unexpected. The σ^+-constants are defined by a linear *free energy* relationship and any attempt to plot activation energy or enthalpy against σ^+ ignores variations in activation entropy behavior as the substituent is changed. Furthermore, the variation of solvent composition raises the question as to whether the σ^+-values are indeed constant. Introduction of the Winstein-Grunwald m**Y** relationship[12] to allow for solvent variation results in an equation of extreme complexity with an excessive number of independent variables of an empirical kind. Although such an extension of the analysis may be appropriate when more comprehensive data are available, it is considered unwarranted at the present time. There can be little doubt, however, that a qualitative relationship does exist between the σ^+ measure of the substituent effect and the extrema behavior of activation energy as predicted by the specific solvation model.

Comparison of *p*-NO_2 and *p*-CH_3 Benzyl Chlorides.—In the specific solvation model interpretation of the extrema behavior of the activation energy it is assumed that in the activation process the composition of the initial state solvation shell undergoes considerable change. The polar initial state is much less specifically solvated by water than the ion-like transition state in ethanol–water mixtures; hence considerable reorganization of the solvation shell is required in the activation process. It may be argued that the relative times of excitation to the transition state and relaxation or reorientation of the solvent molecules are such as to preclude such a change in the composition of the solvation shell in the activation process. On the other hand, there is no evidence to deny the argument that the transition state configuration is attained in a series of steps, perhaps analogous to various levels of vibrational excitation of the rupturing bond. The solvent shell composition might then undergo sequential minor modifications at each of these stages providing, as it were, appropriate solvation stabilization for each vibrationally excited state up to the transition state.

The comparison of the activation parameters associated with the solvolysis of the *p*-nitro- and *p*-methylbenzyl chlorides provides some interesting evidence in favor of the argument that reorganization of the composition of the solvation shell does take place in the activation process. If the group moments[13] associated with the substituents on the benzene ring in both cases are considered for both the initial and transition states of the solvolysis, it is seen that in the activation process the vector direction of the net molecular dipole must invert in the *p*-nitro but not in the *p*-methyl case. The only assumption inherent in this conclusion is that the C–Cl bond length in the transition state has increased from 1.76 Å. to approximately 2 Å. and that the charge development has proceeded to approximately 50% ionic character. Both assumptions appear to be well within reasonable limits. Other combinations of bond extension and charge development will, of course, yield the required inversion of over-all molecular moment vector direction. If the solvation shell of the *p*-nitrobenzyl chloride did not undergo reorganization in the activation process the transition state would be imbedded in the initial state solvent shell which has a dipole vector direction in the opposite sense from that required to stabilize the transition state by dipole-dipole interaction. Accordingly, it would be expected that the activation energy for the *p*-nitro system would be considerably higher than that for the *p*-methyl where no inversion of solute dipole vector takes place. Contrary to this, however, the activation energy for the *p*-nitro system is the *lower* of the two activation energies. This observation casts serious doubt on the possibility that the energy of the transition state of the *p*-nitro system is enhanced by an unfavorably oriented solvation shell. It is probable that the solvolysis of the *p*-nitrobenzyl chloride is not SN1, leading to ions, but even if this were the case there would still be a strong dipolar develop-



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(11) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(12) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(13) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 253.

ment in the C–Cl bond in a more S_N2 like transition state and a similar argument would apply.

The most reassuring observation supporting the solvent reorganization argument is the behavior of the entropy of activation. It has been argued above that the inversion of the net molecular dipole vector direction in the activation process for *p*-nitrobenzyl chloride should result in considerable reorganization of the solvation shell compared with the *p*-methyl case. Although the activation entropies shown in Table II are only approximate in view of the fact that rates and activation energies at the same temperature are not available, there can be little doubt that the greater degree of reorganization in the *p*-nitro case is reflected in the very much larger negative ΔS^* value compared with *p*-methyl. Had the solvent shell change in the activation process been merely one of enhanced electrostriction of a shell of essentially initial state composition due to enhanced polarity of the C–Cl bond, a greater $-\Delta S^*$ value for the *p*-methyl would have been expected.

The comparison of the activation parameters in the two systems and consideration of the various dipole vector changes therefore lend strong support to the argument that solvation shell composition changes do take place in the activation process as assumed in the specific solvation model.

Conclusion

The observed temperature dependence of activation energy behavior for the solvolysis of benzyl chloride in ethanol–water mixtures and the effect of *p*-substitution both lend support to the argument that specific solvation by one or other of the components of the binary solvent system plays an important role in determining the activation parameters associated with reactions in mixed solvents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Hydrolysis Reactions of Halogenated Cyclobutene Ethers: Synthesis of Diketocyclobutenediol[1a]

BY J. D. PARK, S. COHEN[1b] AND J. R. LACHER

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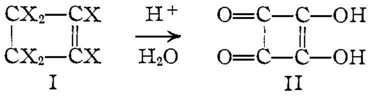
The hydrolysis reactions of 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene and 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene were studied under acidic and basic conditions. Complete hydrolysis of the above compounds resulted in the isolation and identification of diketocyclobutenediol, a new dibasic acid with interesting properties. The anion of this dibasic acid is a member of a series of symmetrical electron delocalized anions, $C_nO_n^{-2}$, representing a new class of aromatic substances. This paper is an extension of a study first reported earlier.[2]

Recently, much interest has been shown in compounds possessing the cyclobutadienoquinone structure since they represent stable molecules with the same formal degree of strain as in the elusive cyclobutadiene, since all four carbon atoms have sp^2 bonding. Cyclobutadiene, however, has never been prepared although its brief existence has been erroneously reported[3] and later shown to be a dimer of cyclobutadiene.[4] Blomquist and Maitlis have recently reported the synthesis of 3,4-dimethylene cyclobutene.[5] Sharts and Roberts[6] have reported cyclohexenyl derivatives of cyclobutadienoquinone.

Prior to this time, only aromatic-substituted derivatives of cyclobutadienoquinone had been prepared.[7]

Roberts has estimated from heat of combustion data that the cyclobutadienoquinone ring system should have a resonance energy (or discrepancy energy using Doering's nomenclature) of 31–60 *kcal.* per mole.[7b,8] This being true, it would therefore seem that cyclobutadienoquinone-type structures should be stable even without resonance stabilization contributions from aromatic substitution.

If this is the case, then diketocyclobutenediol would be the logical end product obtainable from the complete hydrolysis of the cyclobutene ethers according to the scheme where X = halogen and/or alkoxyl



I II

Both Roberts[7a,7b] and Blomquist[7c] prepared their phenylcyclobutadienoquinone compounds by hydrolyzing with concentrated sulfuric acid the fluorine atoms which were allylic to a phenyl group. This also becomes simple chemistry, since $CF_2CH{=}C(C_6H_5)CF_2$ is a vinylog of $-CF_2{-}C_6H_5$. Ben-

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[1] (a) This paper represents part of a thesis submitted by S. Cohen to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, Aug., 1959. (b) Continental Oil Co. Fellow, Ponca City, Okla., 1957–1958.

[2] S. Cohen, J. R. Lacher and J. D. Park, *J. Am. Chem. Soc.*, **81**, 348 (1959).

[3] M. Avram, E. Marica and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959).

[4] M. Avram, C. Mateescu, I. Dinulescu, E. Marica and D. D. Nenitzescu, *Tetrahedron Letters*, No. **1**, 21 (1961).

[5] A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).

[6] C. M. Sharts and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 871 (1961).

[7] (a) E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955); (b) E. J. Smutny, M. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960); (c) A. T. Blomquist and E. A. LaLancette, 135th Meeting, American Chemical Society, Boston, Mass., p. 54-O; *J. Am. Chem. Soc.*, **83**, 1387 (1961); (d) M. P. Cava and D. R. Napier, *ibid.*, **79**, 3606 (1957).

[8] J. D. Roberts, *Record Chem. Prog.*, **17**, No. 2, 95 (1956).