

performing the MINDO/3 calculation. Financial support by the Canadian National Research Council is gratefully acknowledged.

References and Notes

- (1) (a) University of Alberta; (b) The University.
- (2) (a) R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 723 (1968); (b) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 7627 (1972).
- (3) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
- (4) Y. K. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976).
- (5) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 956 (1970).
- (6) F. I. Vilesov and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, **115**, 744 (1957).
- (7) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).
- (8) P. P. S. Saluja, Y. K. Lau, and P. Kebarle, *Can. J. Chem.*, to be published.
- (9) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 5128 (1972).
- (10) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).
- (11) E. F. Caldin and V. Gold, Ed., "Proton Transfer Reactions", Chapman and Hall, London, 1975.
- (12) For a summary of proton affinities and $PA(NH_3) = 202.3$ kcal/mol see P. Kebarle, *Annu. Rev. Phys. Chem.*, **28**, 445 (1977); J. F. Wolf, R. H. Staley, J. Koppel, M. Taagepera, R. T. McIver Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977); D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **98**, 311 (1976). The above proton affinity for ammonia is based on the heat of formation of the *tert*-butyl cation $\Delta H_f(t-C_4H_9^+) = 169$ kcal/mol and $\Delta H_f(H^+) = 367$ kcal/mol. This literature $C_4H_9^+$ value (F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970)) was believed to be well established. Unfortunately this has not proven the case. A recent redetermination of the ionization potential of the *t*-C₄H₉ radical (F. A. Houle and J. L. Beauchamp, reported at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 12–17, 1978) lowers $\Delta H_f(t-C_4H_9^+)$ by ~ 5 kcal/mol. This leads to $PA(NH_3) \approx 207$ kcal/mol, a value proposed some time ago by Franklin (M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2029 (1969)).
- (13) S. K. Pollack, J. L. Devlin, III, K. D. Summerhays, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 4583 (1977).
- (14) K. D. Summerhays, S. K. Pollack, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 4585 (1977).
- (15) $pK_a(m\text{-phenylenediamine}) - pK_a(\text{aniline}) \approx 0.4$ (see ref 16). Thus at room temperature ΔG° for proton transfer from aniline to the diamine is -0.55 kcal/mol. This difference combined with Figure 1, ref 14, leads to $\Delta G \approx \Delta H = -2.1$ kcal/mol.
- (16) J. Vendenbelt, C. Henrick, and S. Vandenberg, *Anal. Chem.*, **26**, 726 (1954); R. Kohn and A. Wasserman, *Helv. Chim. Acta*, **11**, 3 (1928). For other pK_a data see ref 9 in Taft.¹⁴ Actually a range of pK_a values for aniline and *m*-phenylenediamine are available in the literature. These generally show a scatter of $\Delta 0.2$ pK_a units. However, the pK_a difference between aniline and *m*-phenylenediamine is most often ~ 0.4 units.
- (17) The calculations were performed with the MINDO/3 (R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975)) semiempirical method. The calculations involved extensive geometry optimizations. For aniline all geometrical variables were optimized except the distance C–H, which was taken as 1.1 Å (the MINDO/3 distance), and the H–C–C angles, which were assumed to be 120°. For α -naphthylamine all parameters in the ring to which the amino group is attached were optimized as well as all parameters for the amino group. For the other ring, the angles were optimized but the MINDO/3 bond lengths for naphthalene were used. For the protonated species the procedure followed was similar. In the ring-protonated species the HCH angle and distances were optimized but the HCH was assumed normal to the aromatic plane. Complete optimization of the protonated amino group was also made. The heats of formation obtained were: aniline 18.1, N-protonated aniline 165.7, ring-protonated aniline 162.0, 1-naphthylamine 47.9, N-protonated naphthylamine 191.1, ring-protonated naphthylamine 181.0 (all values in kcal/mol). The MINDO/3 calculated heat of formation for the ring-protonated naphthylamine is 10 kcal/mol lower than that for the N-protonated ion. We believed that a difference of 3–4 kcal/mol obtained through the isodesmic processes 6a and 6b is probably more accurate.
- (18) H. Einspahr, J. B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Crystallogr., Sect. B*, **29**, 1611 (1973).
- (19) P. Merlet, S. D. Peyerimhoff, and R. J. Buenker, *J. Am. Chem. Soc.*, **94**, 8301 (1972).
- (20) J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Can. J. Chem.*, **51**, 3242 (1973).
- (21) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3546 (1962).
- (22) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 2222 (1977).
- (23) For detailed discussion of ammonia and methyl substituent effect and a comparison of gas-phase and aqueous basicities see Taft¹¹ and Arnett.¹¹
- (24) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971); P. Kebarle, in "Environmental Effects on Molecular Structure and Properties", B. Pullman Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1976.
- (25) E. M. Arnett, B. Chawla, L. Bell, M. Taagepera, W. J. Hehre, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5729 (1977).
- (26) J. F. Wolf, P. G. Harch, and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 2904 (1975).
- (27) Calculated from data on Figure 1 and eq 12.
- (28) ΔG° for proton transfer given above arrow for gas phase and below arrow for aqueous solution.

The Use of Chlorine Kinetic Isotope Effects for Evaluating Ion Pairing in Nucleophilic Displacements at Saturated Carbon

Donald G. Graczyk,¹ James W. Taylor,^{*2} and Carl R. Turnquist³

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received March 20, 1978

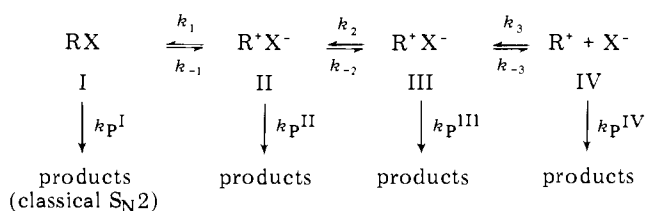
Abstract: Use of the Winstein scheme to describe ion pairing leads to the conclusion that chlorine kinetic isotope effects (KIE) are primarily responsive to processes involving the covalently bound chlorine and less indicative of reactions which occur after the formation of the initial ion pair. This conclusion has been tested by showing that the calculated equilibrium isotope effect (1.0057) and observed ($1.0059_6 \pm 0.0001_1$) KIE are nearly identical when the solvolysis of *p*-methylbenzyl chloride is forced toward a limiting case with 97% trifluoroethanol as solvent. The reaction of *p*-phenoxybenzyl chloride showed similar behavior with an equilibrium KIE value of $1.0058_4 \pm 0.0001_1$. These results suggest that competing ion-pair and S_N2 processes may be one factor contributing to Hammett plot curvature for these nucleophilic displacement reactions. Chloride KIE values for the reaction of *n*-butyl chloride with thiophenoxide anion, where ion pairing does not occur, show little variation with a wide variety of solvents.

Introduction

Evidence has been accumulating which demonstrates that several reversibly formed ion pair intermediates must be considered to interpret the mechanisms of solvolytic displacement reactions at saturated carbon.^{4,5} Shiner and co-workers⁶ have shown that ion pair intervention influences the magnitude of the secondary deuterium isotope effects observed for solvolytic

displacement reactions, and an imaginative study by Murr and Donnelly^{7,8} has demonstrated the feasibility of interpreting the observed, overall isotope effect by considering the isotope effects on each individual process and the overall rate constant for the reaction. Maximum α -deuterium isotope effects occur⁶ when the dissociation of one of the ion pair intermediates (k_2 or k_3 in Winstein's⁴ Scheme I) is rate determining.

Scheme I



The magnitude of this maximum value is characteristic of a particular leaving group and shows a close correspondence to the magnitude of the H-C-X bending force constant in the ground state of the reactant.⁹ This observation suggested to us that perhaps no covalent bonding to the leaving group remains for the ion pair species, II. If this is true, and if the solvent interactions with the ion pairs are similar to those with the free ions, then it may be reasonably expected that there will be no significant leaving group bonding changes and hence no primary leaving group isotope effect for all reactions after species II is formed. This would particularly be true where an atomic fragment is the leaving group, and where rehybridization or geometry changes are not necessary to produce the anionic species. For chlorine as a leaving group, then, only the ionization rate, k_1 , and the rate of return from intimate ion pair, k_{-1} , are expected to contribute to the observed isotope effect if the S_N2 reaction, k_p^{I} , is of negligible importance. It is the purpose of this paper to describe the application of these concepts to the interpretation of chlorine leaving group isotope effects (KIE) on nucleophilic displacement reactions and to provide experimental evidence which examines the validity of these interpretations.

Experimental Section

The techniques used for the determination of the chloride kinetic isotope effects from the substituted benzyl chlorides have been described previously.¹⁰ The normal coordinate analysis and calculation of frequencies for the benzyl chloride ground states were performed with the programs already described.¹¹ The comparison spectra were obtained using a Digilab FTS-20 Fourier transform infrared instrument and verified with a Spex Ramalog laser Raman employing the 6471-Å line of a krypton laser as the source of excitation.

Trifluoroethanol solvent 97% (wt percent) was prepared by mixing 100 g of 2,2,2-trifluoroethanol with 3.1 g of triply distilled water.

***p*-Methylbenzyl chloride** (Aldrich) was distilled, bp 86–87 °C (17 Torr) (lit.¹² by 200 °C (760 Torr)).

***p*-Phenoxybenzyl chloride** was prepared from *p*-phenoxybenzyl alcohol by the procedure of Quelet and Allard¹³ using a reaction time of approximately 30–40 min and was distilled from anhydrous potassium carbonate, bp 124–128 °C (~0.5 Torr). The alcohol was prepared by the addition of formaldehyde gas, generated by heating paraformaldehyde (Mallinckrodt Chemical Works), to the Grignard reagent resulting from 50 g of *p*-bromodiphenyl ether (Aldrich) and 4.8 g of magnesium turnings (J. T. Baker) in anhydrous ether using a modification of the procedure described by Fieser.¹⁴ The product was recrystallized from Skelly B yielding 9.2 g (23%) of fluffy white needles, mp 53–54 °C. Purity and identity of the *p*-phenoxybenzyl alcohol was established by 100-MHz ¹H NMR in CCl₄ solvent using a JEOL MH 100 spectrometer.

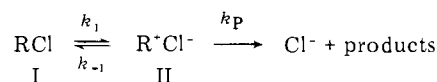
***n*-Butyl chloride** (Aldrich) was purified by the method of Smyth and McAlpine.¹⁵ The purified material boiled at 77 °C (lit.¹⁶ bp 78.4 °C).

Sodium thiophenoxide was prepared by modification of the method of Parker.¹⁷

Anhydrous **methanol** was derived from two sources (Fisher Scientific and Mallinckrodt AR). ***n*-Propyl alcohol** (Mallinckrodt AR) was used as received. ***n*-Amyl alcohol** (Allied Chemical) was shown to be only 60% pure by flame ionization GC peak areas. The impurity is believed to be one of the other amyl alcohols.¹⁸ Because all amyl alcohols have a similar dielectric constant, the mixture of alcohols was not separated, but used as received.

Dimethyl sulfoxide (Me₂SO) (Fisher Scientific), spectrochemical grade, was dried over 4 Å molecular sieves before use. **Dimethyl-**

Scheme II



formamide (DMF) (Eastman Kodak) was Spectro ACS grade. After drying over 4 Å molecular sieves, DMF was vacuum distilled, bp 62 °C (30 Torr) (lit.¹⁹ 153 °C (760 Torr)). **Diglyme** (2-methoxyethyl ether) (Aldrich) was refluxed over sodium metal at reduced pressure and then distilled, bp 54 °C (10 Torr) (lit.²⁰ 159.8 °C (760 Torr)). **Tetraglyme** (tetraethylene glycol dimethyl ether) (Pfaltz and Bauer, Flushing, N.Y.) was refluxed over sodium metal and then distilled at 12 Torr with a head temperature of 144 °C (lit.²¹ bp 276 °C (760 Torr)).

Benzyl chloride (Mallinckrodt AR) was distilled under reduced pressure, bp 62 °C (8 Torr) (lit.²² 63 °C (8 Torr)). Laboratory **distilled water** was further purified by distillation from an alkaline permanganate solution and then again from a sulfuric acid solution in an all-glass still. **Lithium methoxide** (0.2845 M) in methanol was prepared by dissolving 6 g of clean 0.5-in. o.d. lithium rod (Alfa Inorganics) in 3 L of anhydrous methanol (Mallinckrodt) under a dry nitrogen atmosphere.

The kinetics for all the isotope effect studies were obtained at 20.00 ± 0.01 °C. The benzyl chlorides were treated as previously described.¹⁰ For the *n*-butyl chloride study, the reaction was quenched by pouring the reaction mixture into a 100-mL aqueous solution of acid (0.09 M HNO₃) which stopped the reaction by protonating the thiophenoxide anion. The conversion procedure to obtain the chlorine isotopic ratios was similar to one previously described.^{10,23}

Development of Assumptions

For the simple case where only k_1 and k_{-1} are assumed to show a chlorine isotope effect and direct S_N2 displacement is absent, Scheme I can be modified to produce Scheme II.

The rate constant for chloride ion product formation from the intimate ion pair, k_p , will be a function of the rate constants for all the processes following intimate ion pair formation. In addition, because we have assumed that none of these rate constants exhibits an isotope effect, k_p will also exhibit isotopic independence. A steady-state treatment of Scheme II leads to the following expression for the rate of chloride product formation:

$$k = \frac{k_1 k_p}{(k_{-1} + k_p)} \quad (1)$$

The observed isotope effect for this process will then be given by the equation

$$\text{KIE} = \frac{{}^{35}k}{{}^{37}k} = \frac{{}^{35}k_1}{{}^{37}k_1} \cdot \frac{({}^{37}k_{-1} + k_p)}{({}^{35}k_{-1} + k_p)} \quad (2)$$

The observed isotope effect will consist of two factors: one which is given by the KIE on the ionization process, ${}^{35}k_1/{}^{37}k_1$, and one whose magnitude will depend upon the relative rates of product formation and return from the intimate ion pair. If the rate of product formation is very much faster than return ($k_p \gg k_{-1}$), the observed isotope effect will be equal to the ionization KIE and will be diagnostic of the transition state for the k_1 process. The magnitude of this effect may be estimated by means of Bigeleisen's heavy atom approximate expression:²⁴

$$\frac{k_{35}}{k_{37}} = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} \left[1 + \sum G(u_i) \Delta u_i - \sum G(u_i^{\ddagger}) \Delta u_i^{\ddagger} \right] \quad (3)$$

where $u_i = hc \nu_i/kT$; $\Delta u_i = hc \Delta \nu_i/kT$; $G(u_i) = [1/2 - 1/u_i + 1/(e^{u_i} - 1)]$; and h is Planck's constant, k is Boltzmann's constant, c is the speed of light, and T is the temperature in degrees Kelvin.

For the two-center model, which describes the ionization, the $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ term will have a near maximum value larger than unity.²⁵ Also, the second summation inside the brackets in eq

Table I. Rate Constants and Chlorine Leaving Group Kinetic Isotope Effects for Reactions of Substituted Benzyl Chlorides with Solvent Water and Added Salts in Aqueous Acetone at 20 °C (70% Acetone Except as Noted)

substituent	salt	[salt], M	k_1^0, s^{-1}^a	% ROH ^b	$^{35}k/^{37}k^c$
<i>p</i> -CH ₃ O	none		2.38×10^{-4}	100.	$1.0078_6 \pm 0.0000_8$
	NaN ₃	0.050	4.18×10^{-4}	45.5	$1.0087_0 \pm 0.0001_1$
	NaN ₃	0.100	5.87×10^{-4}	28.3	$1.0093_6 \pm 0.0000_8^d$
	NaN ₃	0.149	7.27×10^{-4}	20.2	$1.0098_6 \pm 0.0001_1^d$
	NaN ₃	0.251	9.69×10^{-4}	12.1	$1.0104_3 \pm 0.0000_8^d$
	NaN ₃	0.500	13.79×10^{-4}	5.4	$1.0107_0 \pm 0.0001_1$
	NaC ₆ H ₅ S	0.015	5.88×10^{-3}		$1.0102_1 \pm 0.0001_4$
	NaC ₆ H ₅ S	0.030	11.86×10^{-3}		$1.0103_0 \pm 0.0001_4$
	none ^e		12.07×10^{-4}		$1.0083_0 \pm 0.0001_1$
	none ^f		3.11×10^{-5}		$1.0074_3 \pm 0.0001_4$
<i>p</i> -C ₆ H ₅ O	none		1.63×10^{-6}		$1.0077_6 \pm 0.0001_1$
	NaN ₃	0.010	8.69×10^{-6}		$1.0093_4 \pm 0.0001_1$
	NaN ₃	0.025	1.78×10^{-5}		$1.0095_4 \pm 0.0001_1$
	NaN ₃	0.250	1.20×10^{-4}		$1.0097_1 \pm 0.0001_1$
<i>p</i> -CH ₃	none		9.95×10^{-8}		$1.0070_2 \pm 0.0001_1$
	NaN ₃	0.025	9.09×10^{-6}		$1.0093_5 \pm 0.0001_1$
	NaN ₃	0.064	2.13×10^{-5}		$1.0095_0 \pm 0.0001_4$
	NaN ₃	0.100	3.17×10^{-5}		$1.0094_2 \pm 0.0001_1$
<i>p</i> -H	none		1.31×10^{-8}		$1.0074_2 \pm 0.0001_1$
	NaN ₃	0.100	1.65×10^{-5}		$1.0091_8 \pm 0.0001_1$
	NaN ₃	0.150	2.21×10^{-5}		$1.0092_2 \pm 0.0001_1$
	NaN ₃	0.250	3.44×10^{-5}		$1.0091_8 \pm 0.0000_7$

^a Initial pseudo-first-order rate constant. ^b Corrected to $t = 0$ using the expression in ref 27. ^c Error limits are standard deviation of the mean. ^d Cf. ref 10. ^e 60% acetone solvent. ^f 80% acetone solvent.

3 is expected to be small so that the total term in the brackets, the TDF, will approach its maximum value for the substrate under consideration. The isotope effect on k_1 , arising from the product of these two terms, is clearly expected to be near the maximum observable effect for chlorine-35/37 substitution in the substrate.

Similar considerations allow an estimate of the magnitude of the isotope effect on the k_{-1} process. Because a chemical process involves the same transition state whether it proceeds in the forward or reverse direction, the $\nu_{1L}^\ddagger/\nu_{2L}^\ddagger$ term and the $\Sigma^{3N^\ddagger-7}G(u^\ddagger)\Delta u^\ddagger$ term will be the same for the return process as for the ionization. For k_{-1} , however, the labeled reactant is the free chloride anion and the first summation in the TDF will be small or zero. It follows, then, that $^{35}k_{-1}/^{37}k_{-1}$ should have a value greater than unity but somewhat smaller than the TIF value.¹⁰ As return from the intimate ion pair becomes increasingly important, the second term in eq 2 will decrease from a value of unity when $k_p \gg k_{-1}$ toward a limiting value of $^{37}k_{-1}/^{35}k_{-1}$. Thus, for reactions proceeding through the ionization pathway, the magnitude of the observed chlorine leaving group isotope effect is expected to be diagnostic of the relative amounts of return and product formation from the intimate ion pair. From this analysis, it can be seen that, although the kinetic isotope effects on the k_1 and k_{-1} steps can be related to the transition state for the process, $I \rightarrow II$, in Scheme I, the observed isotope effect on the overall process, $I \rightarrow$ products, may be complicated by a contribution due to partitioning of the intermediate between return and product formation. Indeed, in the limit when $k_{-1} \gg k_p$ (Scheme II), the observed isotope effect, as given by eq 2, will be identical with the equilibrium isotope effect on the process $I \rightleftharpoons II$ and the relationship between transition state and the KIE no longer holds.

Results of Tests of Assumptions

In a previous paper,¹⁰ we suggested that the solvolysis of *p*-methoxybenzyl chloride in 70% aqueous acetone did exhibit characteristics of ion pair formation based on the variation of the observed chlorine KIE as a function of azide concentration. In this case, the increase in KIE from $1.0078_6 \pm 0.0001_0$ to $1.0104_9 \pm 0.0002_5$ as the azide concentration was increased

from zero to 0.25 M was interpreted as signaling a decrease in the relative importance of return from the intimate ion pair (II) by trapping of the intermediate with the azide nucleophile. Subsequently, Collins and co-workers²⁶ measured the carbon and deuterium isotope effects on the reactions of *p*-methylbenzyl chloride and benzyl chloride with azide ion in aqueous acetone at 60 °C and concluded that their observations were not consistent with an ion pair scheme, but rather were indicative of classical S_N2 or competing classical S_N1 and S_N2 processes. In addition, these workers extrapolated their results to include the solvolysis and azide reactions of the *p*-methoxy derivative as well and suggested that the reported azide dependence of the chlorine leaving group KIE could be equally well explained by a shift from a classical S_N2 solvolysis to a classical S_N2 displacement by azide ion.

When we examined several substituted benzyl chlorides under similar conditions to the *p*-methoxybenzyl chloride study, we obtained the data in Table I. For *p*-methylbenzyl chloride and benzyl chloride in the presence of azide, the chlorine KIE values are independent of the azide concentration and are best explained in terms of a classical S_N2 displacement. This result is in agreement with the conclusion drawn by Collins and co-workers.²⁶ Our data on the solvolysis of these compounds also suggest predominantly S_N2 displacement by water, but are insufficient for firm conclusions to be drawn. For the reactions of *p*-phenoxybenzyl chloride, an increasing trend for the chlorine KIE is evident as the azide concentration is increased. A limiting value for the KIE at high azide concentration appears to be about 1.00971 ± 0.00011 , a value not too different from the S_N2 azide values observed with *p*-methylbenzyl (1.0094) and benzyl (1.0092) chlorides. Thus, the azide reaction with *p*-phenoxybenzyl chloride appears to be dominated by S_N2 displacement at high azide concentrations. For the solvolysis of this derivative, and at low azide concentrations, the situation is less clear. It has been reported²⁸ that the solvolysis reaction of *p*-phenoxybenzyl chloride in 70% acetone exhibits considerable S_N1 character as evidenced by the existence of a common ion effect, by values of various thermodynamic parameters, and by salt effects. If this reaction were classically S_N1 (i.e., k_1 in Scheme I rate determining), then one would anticipate a near-maximum chlorine leaving

group KIE value for the solvolysis. The experimental value of $1.0077_6 \pm 0.0001_1$ is smaller than that observed for the S_N2 reaction with azide and clearly does not approximate a maximum value for the *p*-phenoxybenzyl substrate. The relatively small KIE observed for this reaction, which apparently proceeds through an ionization pathway, is better explained in terms of Scheme I. Internal return from the intimate ion pair, as discussed earlier, is expected to lower the observed KIE from that characteristic of the ionization process toward that characteristic of the equilibrium formation of the intimate ion pair from the neutral substrate.

Similar arguments may be applied in the case of the solvolysis of *p*-methoxybenzyl chloride. Thermodynamic parameters for this reaction have been reported²⁹ and were interpreted as characteristic of an ionization process. The observation²⁸ of a common ion rate depression in this reaction is also inconsistent with an S_N2 pathway. Further evidence which can be used to evaluate the probability of an S_N2 displacement by water on *p*-methoxybenzyl chloride in aqueous acetone is provided by the plot of the logarithm of the rate constants for solvolysis in 60, 70, and 80% acetone vs. the Winstein–Grunwald *Y* parameter.³⁰ The plot is linear with a slope of 1.08, which means that the reaction rate is affected similarly to the solvolysis of *tert*-butyl chloride (a classically S_N1 case). S_N2 solvolysis reactions generally exhibit a slope of ~ 0.3 – 0.4 for these plots.³¹ Thus, it seems that the solvolysis of *p*-methoxybenzyl chloride in 70% acetone does not proceed by an S_N2 displacement by water as Collins and co-workers²⁶ suggest. The relatively small chlorine KIE reported for this reaction is better attributed to a lowering of the apparent isotope effect by return from the intimate ion pair. Addition of sodium azide to the reaction mixture results in an increase of the apparent KIE. According to our previous interpretation,¹⁰ this increase is due to an increase in the parameter k_p in eq 2 as a result of an azide displacement on the intimate ion pair, 11.

The possibility remains, however, that a S_N2 reaction with azide also occurs for the *p*-methoxybenzyl chloride substrate. Consideration of the limiting KIE at very high azide concentrations might be expected to test this possibility. If the increase in KIE results only from ion pair trapping, then the limiting KIE should approach the near-maximum value characteristic of the KIE on the process described by k_1 in Scheme I. In contrast, if an S_N2 component is present, very high nucleophile concentrations may cause this component to dominate chloride production, and the limiting value would be the somewhat smaller value characteristic of the S_N2 process. The data in Table I for the reaction of *p*-methoxybenzyl chloride in the presence of 0.5 M NaN_3 suggest that the high concentration limiting KIE may be greater than $1.0107_0 \pm 0.0001_1$, since even at this high azide concentration, approximately 5% hydrolysis still occurs. This value is substantially higher than the purely S_N2 values (1.0092–1.0097) obtained for the other substituted benzyl derivatives, and supports the position that azide serves to trap the ion pair intermediate. However, it is possible that azide reacts with both the intimate ion pair and the neutral substrate, but that the S_N2 reaction does not dominate sufficiently at 0.5 M NaN_3 to control the KIE. At higher azide concentrations, or in the presence of a stronger nucleophile, the converse may be true and this would be subject to experimental test. Significantly higher azide concentrations are precluded for solubility reasons. A change to a stronger nucleophile was therefore tried. Reaction in the presence of very small concentrations of the salt, sodium thiophenoxide, exhibited extremely fast reaction rates relative to the solvolysis reaction. As shown by the rate and isotope effect data in Table I for the reactions with 0.015 and 0.030 M $\text{NaC}_6\text{H}_5\text{S}$, the rate is directly proportional to the salt concentrations, and, significantly, the chlorine KIE values are independent (within

experimental error) of the concentration of added salt. Moreover, the KIE values of $1.0102_1 \pm 0.001_4$ and $1.0103_0 \pm 0.0001_4$ are substantially lower than that observed for the highest azide concentration studied. We conclude that these results with $\text{NaC}_6\text{H}_5\text{S}$ provide convincing evidence for strictly S_N2 reaction between *p*-methoxybenzyl chloride and the thiophenoxide anion. It would be reasonable, on this basis, to expect that the relatively strong azide nucleophile could also react with the neutral substrate via this pathway. The increasing chlorine KIE values observed for higher concentrations of sodium azide are indicative, however, that a substantial portion of the azide reaction proceeds through attack on the intimate ion pair.

From the conclusions drawn during the foregoing discussion, a picture emerges which shows a sensible variation in mechanism with substituent on the benzyl chloride and the nucleophile used. For the reactions of the strongly electron-donating *p*-methoxy substituent, the mechanism appears to shift from strictly S_N2 with the strong thiophenoxide nucleophile to a combination of S_N2 reaction and reaction through the ionization pathway with azide ion, and finally to a reaction with k_p of the same order of magnitude as k_{-1} when the weak nucleophile water is used. Extrapolation of this trend suggests that the reaction could be driven further toward the case where $k_p \gg k_{-1}$ in eq 3 if a very much weaker nucleophile is used, or if a lower concentration of water were employed. The data in Table I demonstrate that when the water concentration is decreased (from 70 to 80% acetone), the isotope effect does indeed decrease, as predicted, from $1.0078_6 \pm 0.0001_0$ to $1.0074_3 \pm 0.0001_4$. Because of the complexity of the *p*-methoxybenzyl chloride system, however, these results must be taken as suggestive rather than conclusive. Too many variable changes, such as solvent polarity, are involved to definitely specify the cause of the change in KIE.

It would be most desirable to study the reaction of an appropriate substrate under conditions where ion pair dissociation is rate determining, and the leaving group KIE could be expected to approach the value characteristic of the equilibrium $I \rightleftharpoons II$ in Scheme I. Shiner and co-workers³² have presented evidence that the solvolysis reactions of *p*-methylbenzyl chloride in aqueous 2,2,2-trifluoroethanol (TFE) mixtures occur with rate-limiting ion pair dissociation. The α -deuterium isotope effects observed for these reactions were very close to the expected limiting value for the chloride leaving group, and Shiner³² attributes this to the strongly ionizing but weakly nucleophilic nature of this solvent.

The chlorine-35/37 equilibrium isotope effect may be conveniently calculated from the normal mode vibrational frequencies, ν_i , for the ground-state molecule and the isotopic shifts for these frequencies, $\Delta\nu_i = {}^{35}\nu_i - {}^{37}\nu_i$, by means of the Bigeleisen heavy atom approximation, as shown in eq 3 using only the $1 + \sum {}^{3N-6}G(u_i)\Delta u_i$ term. Only the ground-state frequencies are needed in the case of isotopic chlorine substitution if the partition function ratio for the free chloride ion is unity. Under this assumption, it is necessary to consider only those vibrational modes which involve motion of the chlorine atom, so that, of the $3N - 6$ frequencies called for in the equation, a smaller number may be sufficient depending upon the symmetry of the molecule studied.

In Table II are listed the observed and calculated frequencies for the vibrational modes sensitive to the motion of the chlorine atom in the *p*-methylbenzyl chloride molecule.³³ The quantity $G(u)\Delta u$ is listed for each frequency at 20 °C, and the equilibrium chlorine isotope effect is calculated as the sum of $G(u)\Delta u$ contributions as between 1.005 73 and 1.005 63.

Experimentally, the observed rate constant for the solvolysis of *p*-methylbenzyl chloride in 97% TFE at 20 °C was $3.47 \times 10^{-6} \text{ s}^{-1}$. The observed chlorine KIE at 20 °C was $1.0059_6 \pm 0.0001_1$.

An analogous experiment was performed using *p*-phenoxybenzyl chloride. The limiting equilibrium isotope effect for this compound should not be very different from that of the *p*-methyl derivative because the ground states of the substituted benzyl chlorides are not particularly sensitive to this small a change in substituent. The KIE found for solvolysis of *p*-phenoxybenzyl chloride in 97% TFE at 20 °C was $1.0058_4 \pm 0.0001_1$. The observed rate constant for this reaction was $1.60 \times 10^{-3} \text{ s}^{-1}$.

Conclusions and Implications for KIE Applications

From the data previously described it appears that the *p*-methoxy compound can be made to exhibit either $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ behavior depending on the nucleophile and that both *p*-methyl and *p*-phenoxy derivatives produce the same equilibrium kinetic isotope effect. In addition, the agreement between the observed equilibrium isotope effects (1.0058_4 for phenoxy and 1.0059_6 for *p*-methyl) and those calculated assuming an ion-pair model (1.0057) suggests that the chloride solvolysis for these two derivatives in 97% TFE can occur by the reaction model of Scheme 1 and that the assumptions involving eq 1 are valid.

Thus, for the very strong thiophenoxide nucleophile, even the *p*-methoxy compound reacts via direct $\text{S}_{\text{N}}2$ displacement. With the somewhat less nucleophilic azide ion, some reaction through the ionization pathway becomes important for the *p*-methoxy derivative and possibly for the *p*-phenoxy derivative, but not for the others. In the solvolysis reactions in 70% acetone, both the *p*-methoxy and *p*-phenoxy derivatives react primarily through the ionization pathway, while the *p*-methyl and unsubstituted compounds probably undergo $\text{S}_{\text{N}}2$ displacement by water. When the solvent is changed to the weakly nucleophilic and strongly ionizing 97% TFE, the *p*-methyl and *p*-phenoxy derivatives react with rate-limiting ion pair dissociation.

These data are not compatible with a simultaneous $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ pathway which does not include an ion-pair step and also explain, in part, some of the disagreement which occurs in the literature when specific experiments are compared as a test for the occurrence of ion pairs. Thus, the results are in agreement with the conclusion of Collins and co-workers²⁶ for the reactions of *p*-methylbenzyl and benzyl chlorides in their solvent and reactant system, but demonstrate that their extrapolation of the $\text{S}_{\text{N}}2$ hypothesis to the reactions of *p*-methoxybenzyl chloride is not justified.

These data also identify one possible factor contributing to the curvature in Hammett plots constructed for nucleophilic displacement reactions on substituted benzyl chlorides.³⁴ A changing mechanism across the series is not the entire answer to this problem, however, because curvature occurs even for reactions which are incontestably $\text{S}_{\text{N}}2$ displacements.³⁵

Based on the spectroscopic data we now have in hand from a number of chlorine-containing aliphatic and aromatic hydrocarbons,³³ we would anticipate that a number of chlorocarbons can be made to show equilibrium isotope effects in the range 1.0050–1.0065. Recently Cromartie and Swain³⁶ have reported equilibrium values for the solvolysis of 2-chloroethanol in various solvents and have suggested that equilibrium between covalently bound chlorine and essentially free chloride ion should result in chlorine isotope effects in the range 1.0053–1.0065. However, the equilibrium isotope effect on the ionization of the R–Cl bond is strongly dependent upon the nature of the substrate and this dependence must be taken into account in predicting the equilibrium isotope effect value to be expected for a given reactant.

In addition to the need for spectroscopic measurements for each substrate to be studied, it is also necessary for the accurate interpretation of chlorine leaving group isotope effects to realize that the same isotope effect may arise in several ways.

Table II. Observed and Calculated Frequencies for *p*-Methylbenzyl Chloride Ground State

measured ^a		calcd ^a		$G(u)\Delta u \times 10^{3b}$
³⁵ ν	$\Delta\nu$	³⁵ ν	$\Delta\nu$	
2866.30	0.0	2866.30	0.01	0.021
1413.70	0.0	1413.69	0.00	0.0
1265.90	0.3	1264.69	0.41	0.686
1039.80	0.8	1040.25	1.08	1.644
724.20 ^c	1.4 ^c	724.28 ^c	1.60 ^c	1.945 ^c
339.25	1.15	339.29	1.17	0.760
2955.80	0.0	2955.74	0.0	0.0
1208.80	0.4	1208.73	0.28	0.459
763.70	0.2	763.71	0.17	0.215
(671.45) ^d	(1.6)			1.842 ^d
$^{35}K_{\text{eq}}/^{37}K_{\text{eq}} = 1 + \sum G(u)\Delta u = 1.00573^{b,c}$				
$^{35}K_{\text{eq}}/^{37}K_{\text{eq}} = 1 + \sum G(u)\Delta u = 1.00563^{b,d}$				

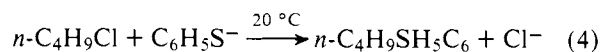
^a Frequencies in cm^{-1} . ^b Evaluated at $t = 20$ °C. ^c For the trans configuration. ^d For the gauche configuration.

Thus, although a chlorine KIE value of approximately 1.0057 for a reaction of *p*-methylbenzyl chloride may be indicative of rate-determining ion pair dissociation, it could as well arise from a direct $\text{S}_{\text{N}}2$ displacement under appropriate reaction conditions. Clearly, the interpretation of the chlorine KIE may be quite complex and requires that as much information as possible be brought to bear for an accurate analysis.

One further complication is the possibility discussed originally by Thornton³⁷ and elaborated on further by Fry and co-workers^{38–40} that compensating solvation of the incipient chloride ion at the transition state may compromise the validity of the chlorine KIE values in describing the degree of carbon–chlorine bonding at the transition state in different solvents. One suggestion by Fry and co-workers^{38,40} was the specific solvation of the transition state may actually lower the kinetic isotope effect values to a significant extent through a mass effect on the leaving group. This possibility was advanced³⁸ to explain the reversal in magnitudes between the calculated leaving group KIE values and the experimentally determined values reported by Grimsrud and Taylor.⁴¹

In order to test the effects of solvation on the chlorine KIE values where ion pairing presumably does not occur, seven pure solvents were employed for the reaction of *n*-butyl chloride with thiophenol anion. These solvents may be classed into three categories: alcohols, ethers, and dipolar aprotic solvents. The alcohols provided a wide range of dielectric constants to measure the bulk or continuum properties of the solvents. Chemical reactivity is known to vary widely in ether solvents,^{42,43} even when the dielectric constant remains essentially unchanged. Dipolar aprotic solvents were chosen to investigate the possible effects of specific solvation without hydrogen bonding at the reaction transition state. These solvents are at least as polar as the alcohols (i.e., $\epsilon > 30$), yet they are incapable of hydrogen bonding to solute molecules.^{44,45}

The model reaction chosen for study is shown in the equation



Equation 4 represents a $\text{S}_{\text{N}}2$ reaction uncomplicated by elimination.⁴⁶

There are six probable solvent interactions which might reasonably be expected to alter transition state structure, and which would be reflected by a change in KIE values. These are (1) solvent–substrate bonding in the transition state with a specific solvent participating as a nucleophile, (2) solvent–leaving group bonding at the transition state, (3) ground-state solvation of the substrate, (4) solvation of the nucleophile, (5) hydrogen bonding with the transition state, and (6) combinations of the above.

Table III. Second-Order Rate Constants and Chlorine Kinetic Isotope Effect Values for the Reaction of *n*-Butyl Chloride Plus Sodium Thiophenoxide in Various Solvents at 20 °C

pure solvent	rate constant ^a	dielectric constant	av KIE value ^b
Aprotic			
Me ₂ SO	2.6×10^{-2}	46.7	1.0096 ₄
DMF	4.1×10^{-2}	36.7	1.0095 ₃
tetraglyme	1.1×10^{-2}	7.7	1.0094 ₂
diglyme	3.5×10^{-3}	7.3	1.0094 ₉
Protic			
methanol	2.2×10^{-5}	32.7	1.0093 ₀
1-propanol	6.2×10^{-5}	20.3	1.0093 ₁
<i>n</i> -amyl alcohol	$\approx 4 \times 10^{-5}$	≈ 14	1.0094 ₂

^a The values tabulated are k_2 (apparent) in L/mol·s. ^b Average of two or more values for each solvent; values estimated to be $\pm 0.0001_s$.

The experimental results obtained for reaction 4 are presented in Table III. Within each class (aprotic and protic) of solvent, slight changes in the rate constant are observed when the solvent dielectric constant is varied. For solvents with high dielectric constants ($\epsilon > 20$), the rate constant changes are in accord with the effect predicted by the Hughes–Ingold electrostatic solvation model⁴⁷ of a charge-dispersed transition state including an anion and a neutral molecule (i.e., the reaction rate will *decrease* with an *increase* in dielectric constant). In solvents with lower dielectric constant ($\epsilon < 15$) the formal (or apparent) rate constant may be low owing to ionic aggregation of the nucleophile which causes the actual nucleophile concentration to be less than that of the formal concentration.⁴⁸

The ether solvent polarity order given by Garst⁴³ is shown to hold for eq 4 in diglyme and tetraglyme, two similar ethers of approximately the same dielectric constant. The difference in rate of approximately a factor of 3 may be attributed to differences in aggregation of the ionic nucleophile between the two solvents.⁴⁹ Ugelstad et al.⁴² found a rate factor of 8.7 in the same direction for the reaction *n*-butyl bromide with sodium phenoxide in the same solvents.

The effect of hydrogen bonding on the rate of eq 4 may be ascertained by comparison of two solvents (aprotic and protic) with similar dielectric constant values, DMF and methanol. The rate constant increases by a factor of ≈ 2000 on going from methanol to DMF. Because the solvent dipole (as measured by the dielectric constant) is approximately the same for these two solvents, the increase in rate for eq 4 may be attributed to an increase in nucleophile activity because the solvent hydrogen bonding of the nucleophile is eliminated in the aprotic DMF solvent.⁵⁰ It is noteworthy that the chlorine KIE values in these two solvents are very close (1.0095₃ vs. 1.0093₀) and near the limit of the experimental uncertainty in the measurements. It is also interesting to note that the chlorine KIE value in the hydrogen-bonding methanol was quite close to the 1.0096₄ value found in Me₂SO, the dipolar aprotic solvent of highest dielectric constant. This indicates that there may be minor and subtle changes at the *n*-butyl chloride–thiophenoxide transition state or ground state or that there is minor hydrogen bonding to the chlorine leaving group. The difference in KIE value between methanol and DMF, which is barely larger than the experimental uncertainty, is consistent with the value observed previously in these laboratories⁵⁰ but is too small to distinguish between these possibilities. The possibility of ground-state solvation differences could be ascertained from the ground-state carbon–chlorine stretching frequencies in the various solvents. Unfortunately, these observations are precluded owing to the strong solvent absorption in the 750–600-cm⁻¹ region of interest.¹¹

The experimental data do suggest that participation of the solvent as a nucleophile in the transition state for this particular reaction is unlikely because variation in KIE value was within experimental error for eq 4 in the dipolar Me₂SO solvent compared to the same reaction in an inert ether solvent, diglyme (1.0096₄ vs. 1.0094₉). In addition, the reaction rate constant did not vary with the fraction of reaction for Me₂SO solvent, indicating that nucleophilic solvent interaction, in addition to the nucleophilic substitution by thiophenol anion, did not occur. We are left, therefore, with the conclusion that for this clearly S_N2 reaction with both a negatively charged entering and leaving group either the solvent properties provide little change in the observed leaving group chlorine KIE or there are compensatory effects which we have yet to uncover. We do note that this conclusion is at variance with that drawn by Cromartie and Swain in a recent study⁵¹ of the entering group chlorine KIE for reactions of ethylene oxide and dimethyl sulfate in protic and aprotic solvents. The conclusions are also at variance with another S_N2 system studied by Saunders and co-workers.⁵² In both of these cases, however, the charge distribution at the transition state is different⁵³ from the reaction discussed here. These discrepancies mean that further investigation into the variation of kinetic isotope effects with solvent properties for S_N1 and S_N2 reactions is clearly warranted.

From the results at hand, without a detailed understanding of the solvent effects, important conclusions may be drawn concerning the response of the chlorine leaving group KIE to ion pairing according to Scheme I. It is clear that the magnitude of the leaving group kinetic isotope effect cannot uniquely define the reaction mechanism, especially when allowance is made for the possibility of S_N2 displacement concurrent with reaction through the ion pairs chain. The magnitude of the leaving group isotope effects on the S_N2 process may range widely depending on nucleophile and substrate structure, and mechanistic assignments made on the basis of a single measured kinetic isotope effect value are likely to lead to erroneous conclusions. On the other hand, the mechanism of the reaction does uniquely determine the magnitude of the observed isotope effect, and with controlled variations in reaction conditions the KIE should be useful in testing mechanistic hypotheses derived on the basis of other probes. In addition, for those reactions which may be shown to proceed with rate-limiting k_1 or those for which only S_N2 displacement is important, the magnitude of the observed isotope effect can be related to the structure of the reaction transition state. For these cases, the promise of insight into the basis of chemical reactivity which spurred early investigations of the kinetic isotope effect phenomenon might be realized.

References and Notes

- (1) From the Ph.D. Thesis of Donald G. Graczyk, University of Wisconsin, Madison, 1975.
- (2) This research has been supported by the National Science Foundation under Grants MPS 73-08429 and MPS 75-21059.
- (3) From the Ph.D. Thesis of Carl R. Turnquist, University of Wisconsin, Madison, 1972.
- (4) Winstein, S.; Appel, B.; Baker, R.; Diaz, A. *Chem. Soc., Spec. Publ.* **1965**, 19, 109.
- (5) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed.; Wiley: New York, N.Y., 1974; pp 247–374.
- (6) Shiner, V. J., Jr. "Isotope Effects in Chemical Reaction", C. J. Collins and N. S. Bowman, Ed.; Van Nostrand-Reinhold: New York, N.Y., 1970; pp 90–159.
- (7) Murr, B. L.; Donnelly, M. F. *J. Am. Chem. Soc.* **1970**, 92, 6686.
- (8) Murr, B. L.; Donnelly, M. F. *J. Am. Chem. Soc.* **1970**, 92, 6688.
- (9) Shiner, V. J., Jr.; Rapp, M. W.; Wolfsberg, M.; Halevi, E. A. *J. Am. Chem. Soc.* **1968**, 90, 7171.
- (10) Graczyk, D. G.; Taylor, J. W. *J. Am. Chem. Soc.* **1974**, 96, 3255.
- (11) (a) Williams, R. C.; Taylor, J. W. *J. Am. Chem. Soc.* **1973**, 95, 1716. (b) *ibid.* **1974**, 96, 3721. (c) Julian, R. L.; Taylor, J. W. *ibid.* **1976**, 98, 5238.
- (12) "Handbook of Chemistry and Physics", 45th ed.; Chemical Rubber Publishing Co.: Cleveland, Ohio, 1964; p C-156.

- (13) Quelet, R.; Allard, J. *Bull. Soc. Chim. Fr.* **1937**, *4*, 1468.
 (14) Fieser, L. F. "Organic Experiments", D. C. Heath: Boston, Mass., 1965; p 90.
 (15) Smyth, C. Y.; McAlpine, K. B. *J. Chem. Phys.* **1935**, *3*, 347.
 (16) Riddick, J. A.; Bunger, W. B. In "Technique of Chemistry", 3rd ed.; Weissberger, A., Ed.; Interscience: New York, N.Y., 1970; Vol. II, p 338.
 (17) Cook, D.; Evans, I. P.; Ko, E. C. F.; Parker, A. J. *J. Chem. Soc. B* **1966**, 404.
 (18) Reference 16, p 660.
 (19) Reference 16, p 446.
 (20) Reference 16, p 214.
 (21) "Handbook of Chemistry and Physics", 51st ed.; Chemical Rubber Publishing Co.; Cleveland, Ohio, 1970; p C-506.
 (22) Heilbron, I. "Dictionary of Organic Compounds", Vol. I; Oxford University Press: New York, N.Y., 1953; p 292.
 (23) Turnquist, C. R.; Taylor, J. W.; Grimsrud, E. P.; Williams, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 4133.
 (24) Bigeleisen, J.; Wolfsberg, M. W. *Adv. Chem. Phys.* **1958**, *1*, 15.
 (25) Bigeleisen, J. *Can. J. Chem.* **1952**, *30*, 443.
 (26) Raaen, V. F.; Juhlke, T.; Brown, F. J.; Collins, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 5928.
 (27) Snee, R. A.; Carter, J. V.; Kay, P. S. *J. Am. Chem. Soc.* **1966**, *88*, 2594.
 (28) Kohnstam, G.; Queen, A.; Ribar, T. *Chem. Ind. (London)* **1962**, 1287, and references cited therein.
 (29) Kohnstam, G. *Adv. Phys. Org. Chem.* **1967**, *5*, 121.
 (30) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.
 (31) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171-219.
 (32) Shiner, V. J., Jr.; Dowd, W.; Risher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4848.
 (33) Julian, R. L. Unpublished results in these laboratories.
 (34) Swain, C. G.; Langsdorf, W. P., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 2813.
 (35) Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1962**, 1062.
 (36) Cromartie, T. H.; Swain, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 545.
 (37) Thornton, E. R. "Solvolytic Displacement Reactions", Ronald Press: New York, N.Y., 1964.
 (38) Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, A. *J. Am. Chem. Soc.* **1977**, *99*, 3371.
 (39) Fry, A. "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed.; Van Nostrand-Reinhold: New York, N.Y., 1970; Chapter 6.
 (40) Sims, L. B.; Fry, A.; Netherton, L. T.; Wilson, J. C.; Reppond, K. D.; Cook, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 1364.
 (41) Grimsrud, E. P.; Taylor, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 739.
 (42) Ugelstad, J.; Berge, A.; Listou, H. *Acta Chem. Scand.* **1965**, *19*, 208.
 (43) Garst, J. F. "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed.; Marcel Dekker: New York, N.Y., 1969; p 555.
 (44) Coniglio, B. O.; Giles, D. E.; McDonald, W. R.; Parker, A. J. *J. Chem. Soc. B* **1966**, 152.
 (45) Rodewald, R. F.; Mahendran, K.; Bear, J. L.; Fuchs, R. *J. Am. Chem. Soc.* **1968**, *90*, 6698.
 (46) Gould, E. S. "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston: New York, N.Y., 1959; p 148.
 (47) Cooper, K. A.; Dhar, M. L.; Hughes, E. D.; Ingold, C. K.; MacNulty, B. J.; Woolf, L. I. *J. Chem. Soc.* **1948**, 2043.
 (48) Heyding, R. D.; Winkler, C. A. *Can. J. Chem.* **1951**, *29*, 790.
 (49) Hirota, N. *J. Am. Chem. Soc.* **1967**, *89*, 32.
 (50) Grimsrud, E. P. Ph. D. Dissertation, University of Wisconsin, Madison, 1970.
 (51) Cromartie, T. H.; Swain, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 2962.
 (52) Hargreaves, R. T.; Katz, A. M.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 2614.
 (53) Westaway, K. C. Private communication, 1977.

A Vibronic Model for Infrared Absorption by a Mixed Valence Anion Radical

Albert H. Schroeder and Stephen Mazur*

Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. Received February 10, 1978

Abstract: The radical anion derived from one-electron reduction of the diketone *cis*-10,11-dimethylsuccindan-9,12-dione (I) behaves as a weakly interacting mixed valence compound. The unpaired electron apparently occupies an orbital derived from weak exchange interaction between the two aryl ketone subunits. This paper concerns interpretation of the unusual infrared absorption spectra of this species. These spectra do not include the characteristic absorptions of either structurally related monoketones or monoketyls. A simplified perturbational model is derived to describe vibrational states associated with C-O stretching motions for weakly interacting ketone and ketyl. The frequency and oscillator strength of the relevant transitions are seen to reflect influences of the exchange interaction, V , and a parameter ΔE_0 which represents distortion of the potential energy surface by dissymmetric solvation and ion pairing interactions. The model is reasonably successful in quantitatively accounting for two of the more unusual bands in the spectra and values of V and ΔE_0 are consistent with other properties of the ion. Of particular interest is the conclusion that these transitions are truly vibronic, not simply vibrational, and that similar behavior should be anticipated for other mixed valence compounds.

Introduction

The class of mixed valence compounds presently encompasses a large number of examples representing extraordinarily diverse structural types.^{1-12,18} Their characteristic feature is the presence of an odd electron associated with a pair of atoms or functional groups which are not directly bonded to one another nor are they in conjugation via π bonds. The odd electron may be symmetrically distributed between the two centers or, in the more common situation, it oscillates back and forth between them at a measurable rate. Experimental studies of these species have usually focused on the rate of intramolecular electron transfer and/or on the characteristic electronic charge-transfer transition, or optical intervalence transition

as it is also known. These phenomena have been adequately described in several theoretical discussions.¹³⁻¹⁶

Vibrational spectroscopy, a particularly valuable tool in analyzing other examples of structurally nonrigid molecules, has been largely neglected in the study of mixed valence compounds. In the few instances where experimental attention has been focused on vibrational properties, the analyses were only very qualitative,^{2,12,17} and we know of no previous theoretical efforts in this area. The present paper deals with vibrational properties of a particular organic mixed valence species, the radical anion II derived from one-electron reduction of dione I. The infrared (IR) spectrum of II was investigated under a variety of conditions and a theoretical model was