

The Photochemistry of Polyhaloarenes. 5. Fragmentation Pathways in Polychlorobenzene Radical Anions

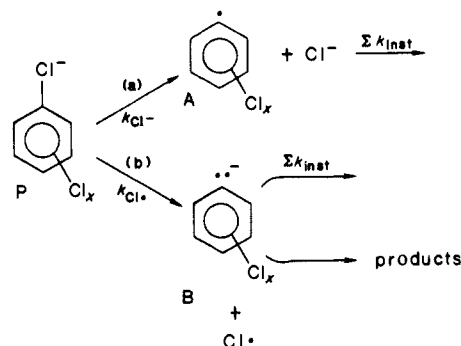
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Abstract: Negative chemical ionization mass spectroscopy of polychlorobenzenes reveals that parent radical anion undergoes fission by two pathways—(a) cleavage to aryl radical plus Cl^- (k_{Cl^-}) and (b) fission to aryl carbanion plus chlorine atom ($k_{\text{Cl}\cdot}$)—and that there is a Hammett relationship between $\log(k_{\text{Cl}\cdot}/k_{\text{Cl}^-})$ and $\Sigma\sigma$. The dependence of the reciprocal of the quantum yield for photochemical dechlorination of trichlorobenzenes through pentachlorobenzene upon the reciprocal of the concentration of the electron donor, triethylamine, was analyzed in order to establish the optimum concentration for radical anion formation. The regiochemistries for the photodechlorination of trichlorobenzenes through pentachlorobenzene in the presence of triethylamine, with and without acetophenone sensitizer, were determined and found to be very similar and quite different from those observed for the direct photolysis in the absence of triethylamine for the comparison cases of 1,2,3,5-tetrachloro- and pentachlorobenzene. The regiochemistry of the fragmentation of polychlorobenzene radical anion to aryl radical plus chloride ion is rationalized in terms of a bent transition state.

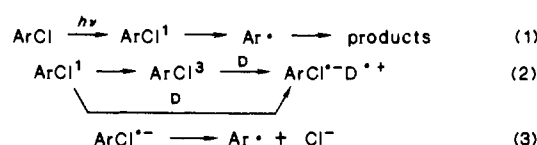
The photodehalogenation of haloarenes is an important process. The reaction has attracted the attention of scientists interested in reaction mechanisms,¹⁻²¹ synthesis,¹⁹ and environmental processes.^{20,22-24} Considerable effort has been devoted to developing

Scheme I



our understanding of the mechanism of photodehalogenation of monohaloarenes^{2-8,12-14,17,18} and in applying this knowledge to synthetic transformations.¹⁹ Since in the environment polyhaloarenes are of more importance than their monohalo parents, we have been interested in applying current theory to developing an understanding of the mechanistic features of the phototransformations of polyhaloarenes.

In the case of chloroarenes the present view of the mechanistic options is that the excited singlet usually (e.g., benzene, biphenyl, and naphthalene systems) possesses sufficient energy to undergo C-Cl bond homolysis, but the triplet state formed by intersystem crossing is generally too low in energy to react in this manner without help in the form of additional thermal energy, exciplex formation, or strain relief. The C-Cl bond homolysis of the singlet generates aryl radical which leads to products (eq 1). Alternatively either the singlet or triplet can react with an electron rich donor molecule (an amine, diene, arene, or sulfide, for example) to produce an exciplex or radical anion/radical cation ion pair (eq 2). The radical anion formed has been viewed as the precursor undergoing fission to aryl radical and chloride ion (eq 3).^{1,19} With polyhaloarenes there would seem to be an important option for the polyhaloarene radical anion that has not been evaluated. For example, a polychloroarene radical anion has two possible modes for bond fission: (a) fission to produce aryl radical and chloride ion or (b) fission to form an aryl carbanion and chlorine atom (Scheme I).



(1) Davidson, R. S.; Goodin, J. W.; Kemp, G. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: London, 1984; Vol. 20, p 191.

(2) Bunce, N. J. *J. Org. Chem.* **1982**, *47*, 1948.

(3) Bunce, N. J.; Gallagher, J. C. *J. Org. Chem.* **1982**, *47*, 1955.

(4) Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; DeGraaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.

(5) Bunce, N. J.; DeSchutter, C. T.; Toone, F. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 859.

(6) Siegman, J. R.; Houser, J. J. *J. Org. Chem.* **1982**, *47*, 2773.

(7) Davidson, R. S.; Goodin, J. W. *Tetrahedron Lett.* **1981**, 163.

(8) Soumillion, J. P.; DeWolf, B. *J. Chem. Soc., Chem. Commun.* **1981**, 436.

(9) Al-Fukhri, K. A. K.; Mowatt, A. C.; Pratt, A. C. *J. Chem. Soc., Chem. Commun.* **1980**, 556.

(10) Choudry, G. G.; Roof, A. A. M.; Hutzinger, O. *Tetrahedron Lett.* **1979**, 2059.

(11) Bunce, N. J.; Kumar, Y.; Ravanal, L.; Safe, S. *J. Chem. Soc., Perkin Trans. 2* **1978**, 880.

(12) Bunce, N. J.; Ravanal, L. *J. Am. Chem. Soc.* **1977**, *99*, 4150.

(13) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 3361.

(14) Bunce, N. J.; Pilon, P.; Ruzo, L. O.; Sturch, D. J. *J. Org. Chem.* **1976**, *41*, 3023.

(15) Åkermark, B.; Baeckström, P.; Westlin, U. E.; Göthe, R.; Wachtmesiter, C. *Acta Chem. Scand.* **1976**, *830*, 49.

(16) Ruzo, L. O.; Zabik, M. J.; Scheutz, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 3809.

(17) Ohashi, M.; Tsujimoto, K.; Seki, K. *J. Chem. Soc., Chem. Commun.* **1973**, 384.

(18) Fox, M.-A.; Nichols, W. C., Jr.; Lemal, D. M. *J. Am. Chem. Soc.* **1973**, *95*, 8164.

(19) Grimshaw, J.; deSilva, A. P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1679. Grimshaw, J.; deSilva, A. P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 857. Grimshaw, J.; deSilva, A. P. *Chem. Soc. Rev.* **1981**, *10*, 181.

(20) Freeman, P. K.; Srinivasa, R. *J. Agric. Food Chem.* **1984**, *32*, 1313. Freeman, P. K.; Jonas, V. *J. Agric. Food Chem.* **1984**, *32*, 1307. Freeman, P. K.; Srinivasa, R. *J. Agric. Food Chem.* **1983**, *31*, 775.

(21) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(22) Bunce, N. J. *Chemosphere* **1982**, *11*, 701.

(23) Crosby, D. G.; Wong, A. S. *J. Agric. Food Chem.* **1981**, *29*, 125. Crosby, D. G.; Moilanen, K. W.; Wong, A. S. *Environ. Health Perspect.* **1973**, *5*, 259. Crosby, D. G.; Hamadmad, N. *J. Agric. Food Chem.* **1971**, 1171.

(24) Choudhry, G. G.; Sundstrom, G.; Ruzo, L. O.; Hutzinger, O. *J. Agric. Food Chem.* **1977**, *25*, 1371.

Table I. Photolysis of Polychlorobenzenes^a in Acetonitrile with TEA^b Present

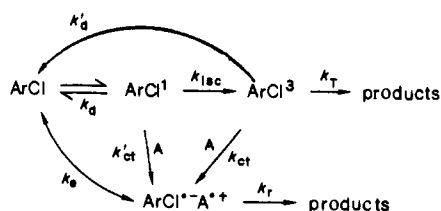
photo products	yield (mol %) ^c				
	1,2,4-TCB	1,2,3-TCB	1,2,3,5-TCB	1,2,3,4-TCB	C ₆ HCl ₅
1,3-DCB	18.19 ± 0.11	46.72 ± 0.25	0.0	0.0	0.0
1,4-DCB	75.25 ± 0.25		0.0	0.0	0.0
1,2-DCB	6.57 ± 0.35	53.28 ± 0.25	0.0	0.0	0.0
1,3,5-TCB			18.77 ± 1.0	0.0	trace
1,2,4-TCB			75.45 ± 1.4	80.12 ± 2.7	trace
1,2,3-TCB			5.78 ± 0.61	19.88 ± 2.7	trace
1,2,3,5-TCB					25.32 ± 0.47
1,2,4,5-TCB					66.21 ± 0.46
1,2,3,4-TCB					8.47 ± 0.06

^a0.05 M in each case. ^b1.5 M. ^cNormalized and average of five runs with standard deviations.

Table II. Sensitized Photolysis of Polychlorobenzenes^a in Acetonitrile with TEA^b Present

photo products	yield (mol %) ^c				
	1,2,4-TCB	1,2,3-TCB	1,2,3,5-TCB	1,2,3,4-TCB	C ₆ HCl ₅
1,3-DCB	21.11 ± 0.37	42.90 ± 1.94	0.0	0.0	0.0
1,4-DCB	72.91 ± 0.40		0.0	0.0	0.0
1,2-DCB	5.98 ± 0.27	57.10 ± 1.94	0.0	0.0	0.0
1,3,5-TCB			22.21 ± 0.71	0.0	trace
1,2,4-TCB			72.94 ± 0.78	83.38 ± 0.79	trace
1,2,3-TCB			4.85 ± 0.47	16.62 ± 0.79	trace
1,2,3,5-TCB					24.33 ± 0.23
1,2,4,5-TCB					69.43 ± 0.33
1,2,3,4-TCB					6.24 ± 0.44

^a0.05 M in each case. ^b1.5 M. ^cNormalized and average of five runs with standard deviations.

Scheme III

than k_s that eq 9 may be simplified to the expression given in eq 10, where the slope of the dependence of $1/\Phi$ upon $1/(A)$ is k_d/Fk_{ct} . With decreasing concentrations of triethylamine [increasing values of $1/(A)$], using eq 9 the plot of $1/\Phi$ vs. $1/(A)$ should be concave downward and flatten out to a slope of zero.

$$\Phi = \frac{k_s}{k_s + k_d + k_{ct}(A)} + \frac{k_{ct}(A)}{k_s + k_d + k_{ct}(A)} \frac{k_r}{k_r + k_e} \quad (8)$$

$$\frac{1}{\Phi} = \frac{k_s + k_d + k_{ct}(A)}{k_s + Fk_{ct}(A)} \quad (9)$$

$$\frac{1}{\Phi} = \frac{1}{F} + \frac{k_d}{Fk_{ct}(A)} \quad (10)$$

This approach was tested with tri-, tetra-, and pentachlorobenzenes. Each polychloroarene was irradiated at 254 nm in acetonitrile in the presence of different concentrations of triethylamine. Quantum yields for product formation were determined in each case by using cyclopentanone as the actinometer and correcting for the light absorbed by the amine.² The reciprocal of the quantum yield was plotted against $1/(A)$ in each case; the results are presented in Figures 2 and 3. An analysis of these plots suggests that an optimum concentration of triethylamine that would assure the predominance of the radical anion over the excited state as product determining intermediate would be one representing a midpoint on the linear positive slope portion of the plot for pentachlorobenzene (1.50 M triethylamine) (Figure 3).

If, instead, one proposes an alternative mechanistic picture in which the triplet or a charge-transfer complex (formed from either singlet or triplet) are product-determining intermediates (Scheme III),² the steady-state assumption leads to eq 11. For the simple case where $k_{ct}' = 0$, equations completely analogous to eq 9 and 10 may be derived. If electron transfer to the singlet state com-

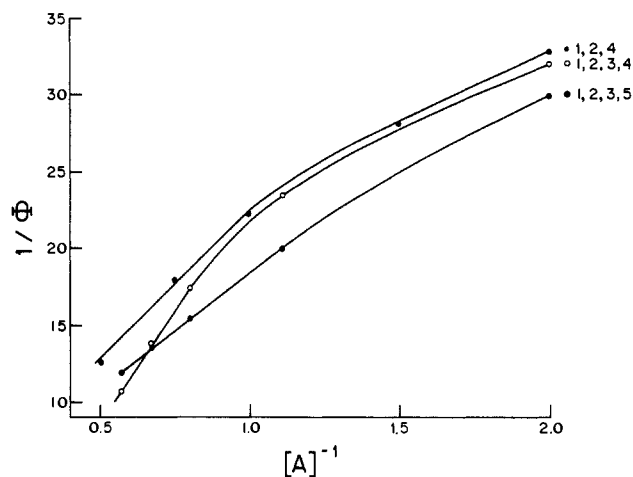


Figure 2. Plot of $1/\Phi$ for 1,2,3,4-tetrachloro-, 1,2,3,5-tetrachloro-, and 1,2,4-trichlorobenzene vs. the reciprocal of the triethylamine concentration.

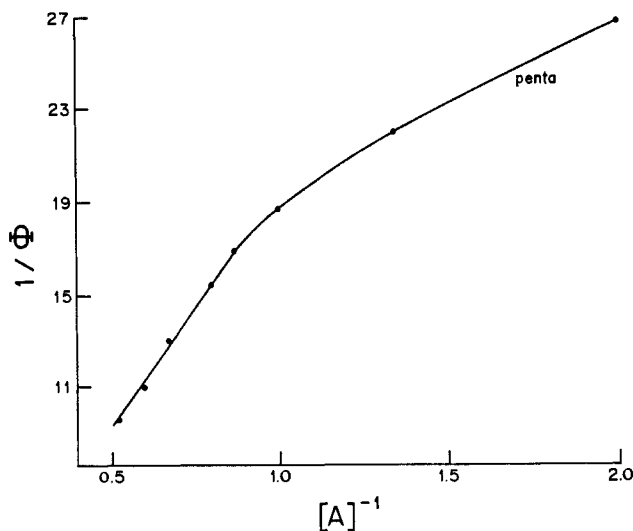


Figure 3. Plot of $1/\Phi$ for pentachlorobenzene vs. the reciprocal of the triethylamine concentration.

Table III. Direct Photolysis of Polychlorobenzenes^a in Acetonitrile in the Absence of Triethylamine

photo products	yield (mol %) ^b	
	1,2,3,5-TCB	C ₆ HCl ₅
1,3,5-TCB	59.24 ± 1.49	
1,2,4-TCB	40.48 ± 1.51	
1,2,3-TCB	0.28 ± 0.01	
1,2,3,5-TCB		67.46 ± 0.85
1,2,4,5-TCB		25.97 ± 0.83
1,2,3,4-TCB		6.57 ± 0.02

^a0.05 M in each case. ^bNormalized and average of five runs with standard deviations.

petes, it is possible that as the amine concentration is increased $Fk_{ct}'(A) \gg k_{isc}$. At this point, a linear expression with a positive slope analogous to eq 10 (k_{ct}' replacing k_{ct}) obtains, while at low concentrations of amine the slope of $1/\Phi$ vs. $1/(A)$ approaches zero. If the singlet state also competes, undergoing fission to products, the kinetic similarity to the picture presented in Scheme II is unaltered.

$$\Phi = \frac{1}{k_{ct}'(A) + k_d + k_{isc}} \left\{ \frac{k_{isc}[k_T + k_{ct}(A)F]}{k_T + k_d' + k_{ct}(A)} + k_{ct}'(A)F \right\} \quad (11)$$

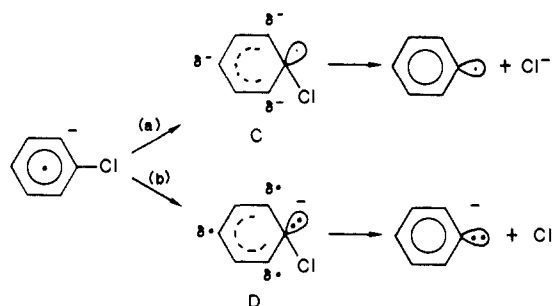
Since the radical anion under consideration could be generated in an alternative manner in a sensitized process without a competing option of direct fission, a very interesting check on the predominance of the radical anion as sole product determining intermediate should be possible. The product compositions for the irradiation of tri- through pentachlorobenzene in the presence of 1.50 M triethylamine with and without acetophenone sensitizer ($E_T = 73$ kcal/mol) are presented in Tables I and II and may be compared with the results of direct irradiation (Table III). The generation of radical anion in the sensitized process is most likely achieved by two competing pathways: (a) energy transfer from triplet sensitizer to substrate chloroarene producing triplet state chloroarene with subsequent electron transfer from triethylamine yielding chloroarene radical anion and (b) reaction of triplet sensitizer with triethylamine to produce an exciplex,²⁸ the radical anion like part serving to reduce the chloroarene to chloroarene radical anion. The latter route is plausible since tertiary aliphatic amines quench triplet ketones at rates close to diffusion controlled,²⁸ however, either route produces the same radical anion.

Discussion

A comparison of the regiochemistries is indeed quite revealing. The product compositions presented in Tables I and II are very similar for all five substrates, suggesting that identical product-determining intermediates are formed from direct and sensitized irradiations in the presence of triethylamine. The regiochemistries of Tables I and II differ sharply with those of the direct irradiation in the absence of electron donor triethylamine, given in Table III, reinforcing the choice of optimum triethylamine concentration used to characterize the radical anion intermediates in the direct irradiations.

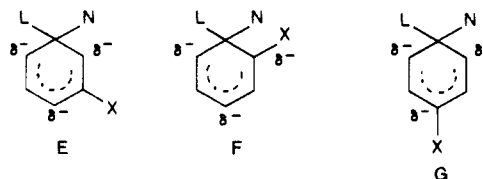
With the regiochemistries established for the radical anions in acetonitrile, it is possible to reconsider the Hammett relationship described in eq 7. Using the σ_o value of Smith and Jones and $\sigma_m^0 = 0.37$ and $\sigma_p^0 = 0.27$ and taking into account the regiochemistry for each substrate, the least-squares slope is 3.91 (intercept = -5.78) with a correlation coefficient of 0.993. If instead σ^r values are employed for the meta and para substituents ($\sigma_o = 0.31$, $\sigma_m^r = 0.37$, and $\sigma_p^r = 0.24$), the slope is 3.98 (intercept = -5.87) with a correlation coefficient of 0.990. It seems clear that corrections for the regiochemistry in the present case of polychlorobenzene substrates are insignificant, which is most likely related to the fact that there is considerable charge dispersal in the carbanion³⁰ as well as the radical anion precursor, so that k_{Cl} is somewhat insensitive to substituent effects, whereas additional chlorine substituents inhibit k_{Cl} by stabilizing the delocalized parent.

A rationale for the regiochemistries observed for the polychloroarene radical anions may be developed by considering the

Scheme IV

transition states for the two competing processes (Scheme IV). The loss of chloride ion in route (a) generates phenyl radical. The transition state for this process would, therefore, be expected to exhibit some radical localization at C-1. The shape of the transition state might be expected to be bent rather than planar, since heterolytic fission of the carbon-chlorine bond in a coplanar transition state would lead to an excited state (a phenyl cation with an extra electron in the π^* molecular orbital), while heterolytic fission of a bent system (such as C) could lead directly to a phenyl radical. Thus, the transition state for route (a) might very well possess some of the character of a delocalized anion with a bent localized radical center (C), while the transition state for chlorine atom loss, by a similar argument, would resemble a delocalized radical with a bent localized carbanionic center (D).

For cleavage processes involving loss of chloride ion, then, we might expect to find similarities in the regiochemistry to that observed by Burdon and co-workers in their studies on nucleophilic aromatic substitution of polyhaloarenes.³¹ Their reactivity patterns have been rationalized by the suggestion that the stability of the Wheland intermediate is decreased by electron pair repulsion³² created by placement of a halogen on a carbon with partial negative charge, with the stability of the intermediate being assessed by determining which intermediate possesses the minimum value for the sum of the charge densities of carbons substituted with halogen in the HOMO (Σc_{ix}^2). This explanation has been termed the I_r repulsion theory and has been successful (with one exception)³³ in rationalizing orientation in aromatic nucleophilic substitution. This approach would predict that the order of stability for the Wheland intermediates below would be $E > F > G$.



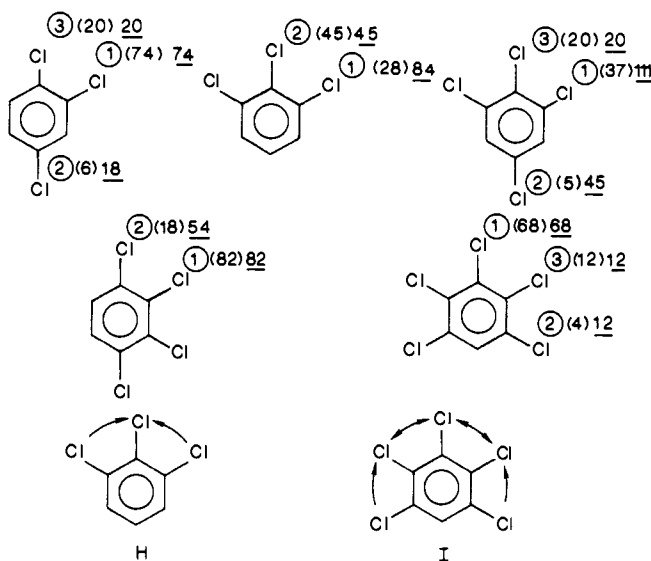
It would appear to be an exciting prospect to apply I_r repulsion theory to our photohydrodehalogenation reactions; however, the accuracy of this comparison depends in part on the radical anions under consideration reacting through transition states of type C. The Hammett plot of Figure 1 illustrates that in the gas phase (with methane as the reagent gas), chloride ion loss is predominant over chlorine atom loss from trichloro- through pentachlorobenzene. Since in route (a) a delocalized radical anion is being converted to a chloride ion, the transition state should involve charge dispersion over these two moieties, while in (b) a delocalized anion is being converted to a somewhat localized phenyl anion, a change to a polar solvent might be expected to cause a shift in mode of fission to route (b). This would only appear to be a problem in the case of pentachlorobenzene, since the ratio of

(31) Burdon, J.; Gill, H. S.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1726. Burdon, J.; Parsons, I. W.; Gill, H. S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1351. Burdon, J.; Parsons, I. W. *J. Am. Chem. Soc.* **1977**, *99*, 7445. Burdon, J. *Tetrahedron* **1965**, *21*, 3373.

(32) Streitwieser, A.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 2444.

(33) Burdon, J.; Childs, A. C.; Parsons, I. W.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 534.

Chart I

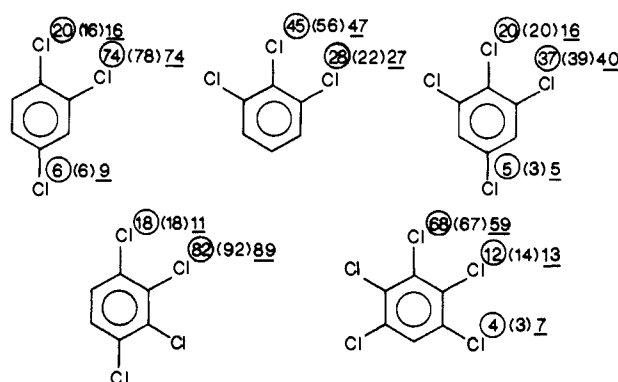


$k_{\text{Cl}}/k_{\text{Cl}}$ is large in all other cases (Figure 1).

Assuming for the purpose of analysis that route (a) is predominant, we would predict the relative rates for reductive dehalogenation described below in Chart I (circled numbers: 1 = fastest, 3 = slowest cleavage rate). By using the data of Tables I and II and correcting for statistical advantages, the observed relative rates for each system are presented in parentheses. The observed relative rates and the predicted relative rates are in agreement for the predominant rate for all systems with the exception of 1,2,3-trichlorobenzene. In this case there would be an extra 2.2 kcal/mol strain relief³⁴ for fission at the central carbon. A correction for strain relief might reasonably be made by using the data of Table III for the direct photolysis of 1,2,3,5-tetrachlorobenzene. Corrected for statistics there is a 3:1 preference for fission at C-2 over fission at C-1, which amounts to a realization of 30% of the available strain relief. With use of this correction, the intrinsic relative rates, within each system, for fission of the C-Cl bond in the radical anions are presented in Chart I (underlined values). In the case of the 1,2,3,5-tetrachlorobenzene isomer the steric correction for comparing fission at C-2 with that at C-5 is 9:1 since two ortho Cl-Cl interactions are relieved at C-2 relative to none at C-5. In the case of pentachlorobenzene, in accord with prediction, the intrinsic rate of fission is highest at C-3. The rates for fission at C-1 and C-2 are equivalent, which is probably the result of a buttressing effect.³⁵ In our standard, with three adjacent chlorines, both Cl-Cl interactions are buttressed on one side only (structure H), while in pentachlorobenzene (structure I) fission at C-1 relieves a singly buttressed interaction, whereas cleavage at C-2 relieves a singly buttressed and a doubly buttressed interaction. Thus, a steric correction greater than 3:1 would undoubtedly be appropriate. This situation is reflected in the 10:1 preference for C-2 over C-1 in the direct photolysis (Table III). This leaves only one wrinkle unresolved and that is in the case of 1,2,4-trichlorobenzene, where there is a tie for second place in intrinsic rate of fission for C-1:C-4. Overall, it appears that this mechanistic approach works very nicely.

Alternatively, one can use the rate data of Chambers et al.³⁶ to calculate the activating effects of chlorine vs. hydrogen in nucleophilic aromatic substitution in benzene systems (ortho:

Chart II



meta:para = 12.1:4.85:1.00). By using these ratios, assuming additivity, the relative rates within each system are calculated and presented in Chart II (numbers in parentheses). Since these reactivities necessarily include a steric factor, it seems reasonable to compare with our statistically corrected relative rates for photochemical fission (circled numbers) at this stage (Chart II). Not only is the order of relative rates in agreement in each polychloroarene, but overall the ratios themselves are in excellent harmony. The striking agreement for pentachlorobenzene suggests that there has not been a change in the mode of fission (a → b in Scheme IV) as a consequence of the change of conditions from the chemical ionization mass spectral runs to liquid-phase conditions in acetonitrile. If there had been a change in mode of fission to route (b), the partial rate factors calculated by Ito et al.³⁷ for the phenylation of chlorobenzene ($f_o:f_m:f_p = 3.09:1.01:1.48$) as well as the results of phenyldefluorination of pentafluorobenzene by Allen et al.³⁸ suggest that the dechlorination pattern observed would have revealed predominant loss at C-2 (C-2 > C-3 > C-1). In addition, substituent rate factors for ortho:meta:para have been calculated by using the data of Tables I and II and minimizing the sum of the squared residuals for observed and calculated relative rates weighted equally for each position. The substituent rate factors obtained, ortho:meta:para = 8.10:4.5:1.0, provide the relative rate pattern illustrated in Chart II with underlined numbers and a very satisfactory fit for this set of polychloroarenes. Thus, it seems quite clear that the regiochemistry of the photofragmentations of polychlorobenzenes that react via radical anions with fission to phenyl radical plus chloride ion is controlled by a transition state closely similar to that generated in analogous nucleophilic aromatic substitutions.

Experimental Section

Mass Spectrometry. Mass spectrometric studies were conducted on a Finnigan 4023 instrument with a 4500 source modification. The Model 625 pulsed positive-negative chemical ionization module was set to the negative ion chemical ionization mode. Methane (Matheson, ultra high purity, 99.97%) was used as the reagent gas in this investigation. The initial Pirani gauge pressure was approximately 0.70 Torr. Samples were leaked into the source via the gas chromatograph inlet at the temperatures specified, 1,2,3-trichlorobenzene (148 °C), 1,2,4- (148 °C), 1,3,5- (148 °C), 1,2,3,5- (173 °C), 1,2,3,4- (123 °C), 1,2,4,5- (123 °C), penta- (103 °C), and hexa- (119 °C), until a gauge reading of approximately 1 Torr was realized. Sample introduction was achieved by placing the compound of interest in an 8 mm × 5 cm tube that had been sealed at one end. This tube was connected to the chemical ionization-gas chromatograph outlet. The air was evacuated from the sample tube by carefully opening the direct chemical ionization interface valve (Precision Sampling microcapillary valve). After the valve was closed, the GC oven was heated to the specified temperature. The valve was then reopened to allow the sample to leak into source.

Photolyses and Nature of Photoreactants. The photolyses of the polychlorobenzenes were carried out in a Rayonet merry-go-round reactor (The Southern New England Co.) equipped with eight 2537-Å Rull

(34) Benson, S. W. In *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976; p 281.

(35) Rieger, M.; Westheimer, F. H. *J. Am. Chem. Soc.* **1950**, *72*, 19. Adams, R.; Hanford, W. E. *J. Am. Chem. Soc.* **1935**, *57*, 1592. Chien, S. L.; Adams, R. *J. Am. Chem. Soc.* **1934**, *56*, 1787. Adams, R.; Yuan, H. C. *Chem. Rev.* **1933**, *12*, 261.

(36) Chambers, R. D. Close, D.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 778. Chambers, R. D.; Waterhouse, J. S.; Williams, D. L. H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 585.

(37) Ito, R.; Migita, T.; Morikawa, N.; Simamura, O. *Tetrahedron* **1965**, *21*, 955.

(38) Allen, K. J.; Bolton, R.; Williams, G. H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 691.

lamps. The temperature of the reactor was maintained at 40 °C by allowing a stream of air to flow through the apparatus during the period of irradiation. Samples (3.0 mL) were placed in quartz tubes (Ace Glass, 170 cm × 15 mm) that were equipped with Pyrex glass sliding stoppers and degassed through 3 or 4 freeze-pump-thaw cycles. The tubes were then sealed in vacuo and irradiated for 30 min. Quantum yields of the photoproducts were determined with cyclopentanone as the actinometer. Acetophenone was used as the sensitizer, and the yields (mol %) of products were determined with dodecane as an internal standard.

Ultraviolet and NMR studies were carried out over a wide range of pentachlorobenzene concentrations to determine if a ground-state charge-transfer complex with triethylamine is formed. There was no evidence for a charge-transfer complex with either spectral technique.

Product Analyses. The photolysis mixtures were analyzed by gas chromatography on a Varian 3700 gas chromatograph equipped with a flame ionization detector. A 6-ft column, 15% Carbowax (20 M) supported on Chromosorb P, AW/DMCS (60/80 mesh), was used. The temperature of the column was programmed from 90 °C for 18 min to 180 °C at 5 deg/min., while the helium gas flow was 30 mL/min; the injector port and the detector temperatures were maintained at 180 and 240 °C, respectively. These conditions were found to be most suitable,

especially for resolving the peaks for 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes. Also, of all the stationary phases and supports tried, Carbowax (20 M) and Chromosorb-P proved to be the best choice for this purpose. The photoproducts were identified by comparing their gas chromatographic retention times with those of the known compounds and by mass spectrometry. The MS analyses were carried out on a Finnigan 4023 mass spectrometer equipped with a Finnigan 9610 gas chromatograph.

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Registry No. 1,3-DCB, 541-73-1; 1,3-DCB (radical anion), 63697-17-6; 1,4-DCB, 106-46-7; 1,4-DCB (radical anion), 55232-43-4; 1,2-DCB, 95-50-1; 1,2-TCB (radical anion), 34531-00-5; 1,3,5-TCB, 108-70-3; 1,3,5-TCB (radical anion), 63697-19-8; 1,2,4-TCB, 120-82-1; 1,2,4-TCB (radical anion), 63697-18-7; 1,2,3-TCB, 87-61-6; 1,2,3-TCB (radical anion), 51703-47-0; 1,2,3,5-TCB, 634-90-2; 1,2,3,5-TCB (radical anion), 63697-21-2; 1,2,4-TCB, 95-94-3; 1,2,4,5-TCB (radical anion), 63697-22-3; 1,2,3,4-TCB, 634-66-2; 1,2,3,4-TCB (radical anion), 63697-20-1.

A Method of Transition-State Mapping for Arenesulfonate Leaving Groups

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Abstract: Equilibrium data for methyl transfer between arenesulfonate groups can be plotted vs. rate data in Brønsted-type plots to give $\beta_{\text{lg}}^{\text{CH}_3}$. This parameter measures the extent of arenesulfonate loss at the transition state. Its use in transition-state mapping is demonstrated for several elimination and substitution reactions.

The development of methods for characterizing the transition states of organic reactions has been a primary goal of organic chemists for decades. The most simple and perhaps the most informative structural feature of the transition state of a reaction is the extent of bond breaking and/or bond making that has occurred. For multibond reactions the bond making and bond breaking are not necessarily linked, and each can proceed to different extents at the transition state. The relationship between bonding change and the energy of the transition state has been developed by the use of More-O'Ferrall-Jencks (MOFJ) diagrams,¹ which are three-dimensional reaction-coordinate diagrams. Two dimensions are used to express bonding changes that occur during the reaction, and the third is reserved as an energy coordinate.² MOFJ diagrams are quite useful as a graphical representation of the transition-state structure, and they are also very useful in predicting changes in transition states which will occur as a result of structural changes that are made in the reactants.³ Thus MOFJ diagrams have proven to be an important conceptual tool in understanding relationships between reactivity, selectivity, and transition-state structure.^{1,4}

The utilization of MOFJ diagrams in describing transition-state structures has largely been qualitative. In order to precisely locate the transition state on the energy surface, parameters are needed to accurately describe chemical bonding at the transition state. These can be plotted as coordinates in the MOFJ diagram, thereby locating the transition-state structure on the energy surface. Many important transition-state probes, such as Hammett ρ and isotope effects ($k_{\text{H}}/k_{\text{D}}$ or others), are not suitable for this purpose. The inherent disadvantage of these parameters is that the upper limits they can take are not well-defined. Thus the boundaries of the energy surface over which the transition state can move are not known. For example, parameters measuring charge buildup are not necessarily related to bond breaking.⁵ Kinetic isotope effects are more directly related to bond-breaking processes; however, theoretical models must be used to establish the upper limits. In general, uncertainties in the model calculations cause the maximum values to be uncertain for many heavy-atom isotopes.⁶ Furthermore, kinetic deuterium isotope effects are rendered uncertain by contributions of tunnelling.⁷

An attractive and convenient way to quantitate the extent of bonding change at the transition state for proton transfers is to

(1) (a) More-O'Ferrall, R. A. *J. Chem. Soc. B* 1970, 274. (b) Jencks, W. P. *Chem. Rev.* 1972, 72, 705. (c) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* 1977, 99, 7948.

(2) These changes can be formulated in more than three dimensions; however, they are rarely encountered.

(3) (a) Grunwald, E. *J. Am. Chem. Soc.* 1985, 107, 125. (b) An excellent discussion of these diagrams is: Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981; pp 199-206.

(4) (a) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* 1979, 101, 3295. (b) Harris, J. M.; Paley, M. S.; Prasthofer, T. W. *J. Am. Chem. Soc.* 1981, 103, 5915. (c) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* 1979, 101, 3288.

(5) (a) Johnson, C. D. *The Hammett Equation*; Cambridge University: Cambridge, 1973; p 152. (b) See, for example: Bernasconi, C. F.; Gandler, J. F. *J. Am. Chem. Soc.* 1979, 101, 3295.

(6) (a) Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; Chapter 9, p 258. (b) Hasan, T.; Sims, L. B.; Fry, A. *J. Am. Chem. Soc.* 1980, 105, 3967. (c) Koch, H. F.; McLennan, D. J.; Koch, J. G.; Tumas, W.; Dobson, B.; Koch, N. H. *J. Am. Chem. Soc.* 1983, 105, 1930. (d) Keefe, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* 1983, 105, 265. (e) Brown, K. C.; Romano, F. J.; Saunders, W. H., Jr. *J. Org. Chem.* 1981, 46, 4242.

(7) (a) Reference 6a, p 36. (b) Kresge, A. J. *J. Am. Chem. Soc.* 1980, 102, 7779 and references therein.