and photosensitized[9-12] reactions. *Thus the pressure decrease observed in the photolysis of Chd is the result of polymer formation by a reaction which has no parallel in the thermal reactions of Chd.*

The arguments in favor of internal conversion in the photolysis of Chd may be summarized as follows. (a) The decomposition reaction of Chd to acetylene and ethylene may be common to both the photolysis and the pyrolysis and might therefore proceed from the same vibrational levels of the ground electronic state in both cases.[14] (b) The calculated lifetime for Chd molecules in S_1 (4×10^{-9} sec)[2-4] is presumably too short to account for the observed pressure dependence of some product yields. (c) Chd fluorescence has not been observed even under extreme conditions.[15]

Taking into consideration the high quantum yield of the photoisomerization of Chd to 1,3,5-hexatriene in the liquid phase (0.40),[16] the different nature of the thermal and photochemical steps leading to H_2 + benzene, the absence of polymer formation in the gas-phase thermolysis, and the absence of dimer formation in the gas phase photolysis, it is concluded that internal conversion of electronically excited singlet-state molecules may not be as important in the photolysis of Chd as deduced from the earlier work.

One of the referees has asked us to speculate what might be happening in the photolysis of Chd. It is possible that the pressure dependence of the class II products is the result of one of the following.

(1) The products are formed after internal conversion as postulated by Srinivasan. In this case only very high vibrational levels are involved thus giving rise to products that differ from those observed in normal pyrolysis studies. Deactivation does not progress stepwise (otherwise the dimers should be formed) but in one or two collisions. It is possible that the reactions of these high vibrational levels might be observed in shock-tube studies.

(2) The class II products are formed from an upper triplet state of Chd which is reached by intersystem crossing. This triplet state has a configuration which does not permit it to phosphoresce nor can it be vibrationally deactivated to the lowest triplet state (otherwise the dimers typical of triplet photosensitization should be observed). Once again colllsional deactivation has to take place in only one or two collisions rather than in a stepwise fashion.

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[14] P. Datta, T. D. Goldfarb, and R. S. Boikess (*J. Amer. Chem. Soc.*, **93**, 5189 (1971)) concluded that the absence of absorption bands due to benzene, ethylene, and acetylene in the photolysis of matrix isolated Chd (20°K) is consistent with the suggestion that these products arise *via* internal conversion to vibrationally excited ground states. As pointed out above, however, the thermal route to formation of benzene is not unimolecular decomposition of excited Chd to benzene + H_2 as proposed by Srinivasan for the photolysis.

[15] R. J. De Kock, Doctoral Thesis, Rijksuniversiteit te Leiden, 1959, p 66.

[16] Reference 12, p 72. The quantum yield of this isomerization, which is presumably a reaction of the electronically excited singlet state, is probably as high in the gas-phase photolysis. Srinivasan[3] reported 0.13 for the quantum yield of 1,3,5-hexatriene formation at 4.75 Torr Chd pressure. He pointed out that the quantum yield must be dependent on irradiation time as well as other factors.

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Kinetic Arguments for the Existence of Hydrogen Bonded Carbanion Intermediates during Dehydrohalogenation Reactions of $C_6H_5CHClCF_2Y$

Sir:

One experimental technique often used to look for carbanion intermediates during 1,2 elimination reactions is to see if the hydrogen atom, which is eventually lost, will exchange with bulk solvent prior to the formal elimination process.[1,2] Since there is current interest in whether or not base-initiated 1,2 eliminations are concerted,[3] we wish to report some kinetic results which strongly suggest that the dehydrochlorination of $C_6H_5CHClCF_2Cl$ proceeds through a carbanion intermediate even though exchange of the benzylic proton does not occur prior to the elimination process. The results of our kinetic studies and relevant previous work on β-phenylethyl halides[4] are summarized in Table I.

Table I. Relative Rates, Activation Parameters, and ρ Values of Dehydrohalogenation and Detritiation Reactions with Ethanolic Sodium Ethoxide

Compound	Process	Rel rate,[a] 25°	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] eu	ρ[b]
$C_6H_5CHClCF_3$	-HF	17	28.4	8.6	3.73[c]
$C_6H_5CDClCF_3$	-DF[d]	39	28.0	9.1	
$C_6H_5CTClCF_3$	Detrit	222	27.0	9.1	3.94[c]
$C_6H_5CTClCF_3$	Detrit[d]	507	26.6	9.2	
$C_6H_5CHClCF_2Cl$	-HCl	5.5×10^6	19.7	4.7	3.94[c]
$C_6H_5CH_2CH_2F$[f]	-HF	1[e]	25.3	−5.4	3.12
$C_6H_5CH_2CH_2Cl$[f]	-HCl	80	23.2	−5.6	2.61

[a] Activation parameters calculated from at least four temperatures over a 30° range using the ACTENG program (D. F. DeTar, "Computer Programs for Chemistry," Vol. III, W. A. Benjamin, New York, N. Y., 1969, p 6). The program also calculated rates for all reactions at 25°. [b] Correlation coefficients for both literature and our plots are better than 0.994. [c] Substituents used were *p*-CH_3, *m*-CH_3, H, *p*-Cl, and *m*-Cl. [d] EtOD solvent. [e] Extrapolation of data from ref 4 gave a value of $k = 4.36 \times 10^{-8}\ M^{-1}\ \text{sec}^{-1}$ at 25°. [f] Data from ref 4.

The presence of an α chlorine and two β fluorines should substantially increase the acidity of the benzylic hydrogen, and the 68,000-fold faster rate for dehydrochlorination of $C_6H_5CHClCF_2Cl$ (I) than $C_6H_5CH_2CH_2Cl$ (II) was not unexpected in a process that requires base attack on the hydrogen. The surprising result was that the elimination of HF from $C_6H_5CHClCF_3$ (III) was only 17 times faster than from $C_6H_5CH_2CH_2F$ (IV). One explanation for the discrepancy could be that reactions of I, II, and IV proceed through standard E2 mechanisms while the elimination of HF from III proceeds through an intermediate carbanion. Our studies of ethoxide reactions with fluoroalkenes suggest that fluoride ion is a poorer leaving group when it comes from a trifluoromethyl group rather than a less highly fluorinated group.[5,6] This

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[1] J. Hine, R. Wiesboeck, and O. B. Ramsey, *J. Amer. Chem. Soc.*, **83**, 1222 (1961).

[2] P. S. Skell and C. R. Hauser, *ibid.*, **67**, 1661 (1945).

[3] F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

[4] C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2535 (1960).

[5] H. F. Koch and A. J. Kielbania, Jr., *ibid.*, **92**, 729 (1970).

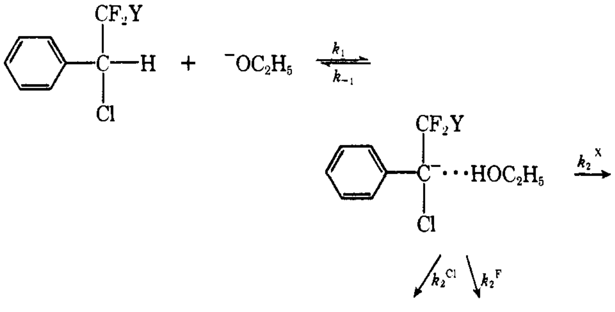
[6] H. F. Koch, A. G. Toczko and J. G. Koch, Abstracts of the 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971.

seems reasonable since the C–F bond becomes stronger with an increasing number of fluorines bonded to the same carbon atom and could therefore readily account for a switch in the mechanism of dehydrofluorination when going from IV to III.

A mechanism which involves a carbanion intermediate for the elimination of HCl from I, however, cannot be excluded, and we therefore studied both primary isotope effects and isotopic exchange reactions of benzylic hydrogens for both I and III. When I was subjected to ethoxide in EtOD, unreacted starting material was found to contain no deuterium. A similar result has been reported for β-phenylethyl bromide.[2] Since exchange of the benzylic hydrogen does not occur, the primary isotope effect for dehydrochlorination was determined directly by running $C_6H_5CDClCF_3$ in EtOH and comparing it to I. The effect at 0°, k_H/k_D = 2.8, was only 30–35% of that calculated by extrapolating Saunders' data for $C_6H_5CD_2CH_2Br$ and $C_6H_5CH_2CH_2Br$.[7] This low k_H/k_D value suggests that the reaction is either proceeding through a highly unsymmetrical transition state or that an intermediate carbanion, which has internal return to starting material, is being formed prior to chloride ion ejection. Since exchange of the benzylic proton of III is faster than the elimination reaction, it was necessary to measure elimination from $C_6H_5CDClCF_3$ in EtOD and make an appropriate correction for the solvent isotope effect. Detritiation kinetics were carried out in both EtOH and EtOD and a solvent isotope effect of 2.3 was calculated. This value is consistent with the literature.[8] Applying this correction resulted in a negligible primary kinetic isotope effect for dehydrofluorination at 25° and this is consistent with the formation of a carbanion that has substantial internal return prior to loss of fluoride.[8] Table I contains ρ values from five point Hammett σ–ρ plots for the elimination of HCl and HF and the detritiation reaction. A similar plot for the reaction of ethoxide with $C_6H_5CCl{=}CF_2$ in ethanol gave a ρ of 3.94. These high positive values point to a large development of negative charge in the transition state of all four reactions.[9] This fact coupled with the small primary isotope effects lead us to the conclusion that all four reactions are proceeding through carbanion intermediates.

The differences in the effects of a $-CF_3$ *vs.* a $-CF_2Cl$ group on either the acidity of the hydrogen or on the stabilization of a carbanion intermediate should be small.[10,11] We therefore propose a single mechanism (Scheme I) for the various reactions of our system. The initial reaction of ethoxide with the benzylic hydrogen would lead to the formation of a strong hydrogen bonded species between the carbanion and the solvent molecule formed during the reaction. It has been experimentally demonstrated that neutral carbon is a good hydrogen bonding base and suggested that carbanions should be excellent in that capacity.[13] The loss of chloride can come directly from this intermediate (k_2^{Cl}), while the hydrogen bond must be broken to allow exchange with bulk solvent (k_2^X). The activation energy for exchange of III-*t* is about 28 kcal/mol, and we see no reason why it should be less for I. Since the activation energy for dehydrochlorination is only 20 kcal/mol, the exchange process cannot compete favorably with the loss of chloride. The same type of argument can be made to support the postulated intermediate for reactions of III, since the benzylic proton should have the same order of reactivity as in I and much greater than in IV. In the ethoxide-catalyzed reaction of III, k_{-1} is apparently much larger than k_2^X, which is greater than loss of fluoride (k_2^F), and the kinetic results thus clearly show that in this case the effects of internal return can be quite substantial. Still unanswered is whether or not internal return from the postulated intermediate in the reaction of I is favored over loss of chloride. Further work is being carried out to attempt to answer this by making use of a method recently published by Streitwieser[14] and by looking at the chlorine isotope effect.[15]

Scheme I



$$k_2^{Cl}(Y = Cl) >>> k_2^{x} > k_2^{F}(Y = F)$$

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(7) W. H. Saunders, Jr., and D. H. Edison, *J. Amer. Chem. Soc.*, **82**, 138 (1960).

(8) A. Streitwieser, Jr., J. A. Hudson, and F. Mares, *ibid.*, **90**, 648 (1968).

(9) A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

(10) W. A. Sheppard, *Tetrahedron*, **27**, 945 (1971).

(11) Kinetic evidence for this is given in ref 5. Further confirmation comes from kinetic studies on reactions of ethoxide with $C_6H_5CR{=}CFCl$ in ethanol, where rates are the same for R = $-CF_3$ or $-CF_2Cl$.[12]

(12) H. F. Koch and R. L. Decker, Jr., unpublished results.

(13) L. L. Ferstandig, *J. Amer. Chem. Soc.*, **84**, 3553 (1962).

(14) A. Streitwieser, Jr., W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmake, C. J. Chang, and T. L. Kruger, *ibid.*, **93**, 5096 (1971).

(15) A review of using various isotope effect studies in elimination reactions has just appeared: A. Fry, *Chem. Soc. Rev.*, **1**, 163 (1972).

(16) (a) Supported by NSF-URP Grant GY-7413 during the summer of 1970. (b) Supported by NSF-URP Grant GY-9839 during the summer of 1972.

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Bridgehead Halogen Exchanges

Sir:

Nucleophilic substitutions at bridgehead positions of small bicyclic ring systems are well known to require vigorous reaction conditions.[1] Classical results with 1-halobicyclo[2.2.1]heptane derivatives established that

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(1) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); (b) V. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960); (c) D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).