

Reaction of Halogenoacetylenes with Sulphur Nucleophiles studied by Extended Hückel Molecular Orbital theory

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Extended HMO calculations have been carried out for the reactions of 1-halogeno-2-methyl- and 1-halogeno-2-phenylacetylenes with HS⁻, in order to compare different positions of attack by the nucleophile (C-1, C-2, or halogen). Potential energy surfaces in the region of possible reaction intermediates have been obtained, and some definite minima have been found. Attack at C-1 appears to be favoured when halogen is F or Cl for both alkyl and aryl derivatives. Computations favour halogen attack in the case of iodo(phenyl)acetylene. Both kinds of attack seem possible for bromo(phenyl)acetylene. These results compare well with the outcome of experiments.

THREE main mechanistic proposals have been advanced for the nucleophilic substitution of halogenoacetylenes (Scheme). The mechanism of addition to the α -carbon atom and elimination (a), proposed by Miller *et al.*,¹ is analogous to the most common mechanism for nucleophilic substitution at olefinic and aromatic carbon atoms. Mechanism (b), suggested by Arens,² involves nucleophilic attack on the halogen; it gives the same products as mechanism (a) in aprotic solvents only, since protic solvents rapidly protonate the intermediate carbanion. Route (c), proposed by Viehe *et al.* for alkylhalogeno-

acetylenes,³ comprises an addition to the β -carbon atom, followed by α -elimination and migration of the nucleophile, through an 'onium' dipolar structure. The scope of each mechanism has been discussed.⁴

Kinetic studies were mainly performed in the case of arylhalogenoacetylenes for reactions with phosphorus,⁵ oxygen,⁶ nitrogen,⁷ and sulphur^{1,8} nucleophiles. Evi-

⁴ (a) S. Y. Delavarenne and H. G. Viehe, 'Chemistry of Acetylenes,' ed. H. G. Viehe, Dekker, New York, 1969, p. 691; (b) L. Brandsma, H. J. T. Bos, and J. F. Arens, *ibid.*, p. 767.

⁵ (a) A. Fujii and S. I. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 3694; (b) J. I. Dickstein and S. I. Miller, *J. Org. Chem.*, 1972, **37**, 2168.

⁶ R. Tanaka, M. Rodgers, R. Simonaitis, and S. I. Miller, *Tetrahedron*, 1971, **27**, 2651.

⁷ J. I. Dickstein and S. I. Miller, *J. Org. Chem.*, 1972, **37**, 2175.

⁸ (a) M. C. Verploegh, L. Donk, H. J. T. Bos, and W. Drenth, *Rec. Trav. chim.*, 1971, **90**, 765; (b) P. Beltrame, P. L. Beltrame, M. G. Cattania, and M. Simonetta, *J.C.S. Perkin II*, 1973, 63.

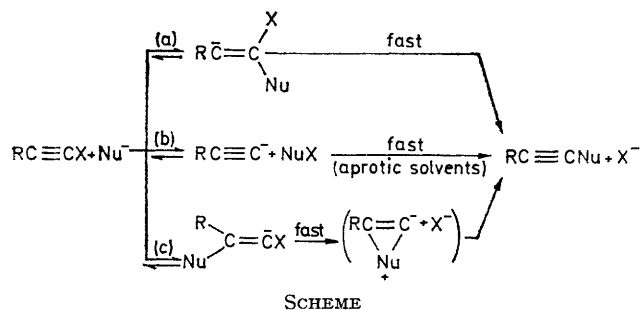
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¹ A. K. Kuriakose and S. I. Miller, *Tetrahedron Letters*, 1962, 905.

² J. F. Arens, *Rec. Trav. chim.*, 1963, **82**, 183.

³ H. G. Viehe, *Angew. Chem. Internat. Edn.*, 1967, **6**, 767; H. G. Viehe and S. Y. Delavarenne, *Chem. Ber.*, 1970, **103**, 1216.

dence was found for mechanisms (a) and (b). Several factors (nucleophile, solvent, leaving group) decide whether the reaction follows one or other of these mechanisms, or whether they operate concurrently. In



particular, for the more polarizable (P,S) nucleophiles the dependence on the nature of the leaving group seems to be critical.

We thought it interesting to examine some aspects of these reactions by means of extended HMO calculations. These were done for the systems $\text{MeC}\beta\equiv\text{C}\alpha\text{X} + \text{HS}^-$ and $\text{PhC}\beta\equiv\text{C}\alpha\text{X} + \text{HS}^-$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$).

Outline of the Method.—Extended Hückel theory⁹ seemed to us a suitable tool for a problem of this size, being the cheapest MO formulation to have proved successful in the calculation of reaction surfaces.¹⁰ Owing to the very large number of parameters to be taken into account, the description of the reaction path could be undertaken only if large approximations were made. First, the nucleophilic reagent was the simple thiolate anion HS^- ; the methyl and phenyl groups were always in a fixed conformation. The progress of the reaction was visualized by building the potential energy surface over which the sulphur atom moved in the surroundings of the acetylene molecule. In doing so, a realistic guess was needed for the behaviour of the acetylene; a model was assumed and is sketched in Figure 1. Attempts to minimize the energy of the

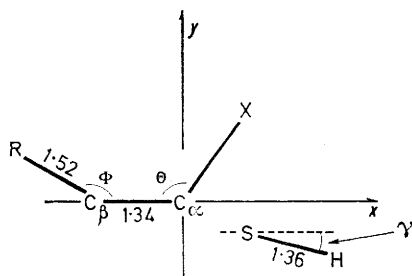


FIGURE 1 Geometrical constants and variable parameters for halogeno-(methyl)- and -(phenyl)-acetylenes and the HS^- ion.

$\text{R} = \text{Me}$: $\text{C}-\text{H}$ 1.1 Å, HCH 109.5°. $\text{R} = \text{Ph}$: $\text{C}-\text{C}$ 1.4 Å, $\text{C}-\text{H}$ 1.07 Å, all angles 120°

molecule as a function of internal parameters failed, owing to the tendency of the triple bond length to collapse to zero. This failure is consistent with the results obtained for acetylene itself⁹ using extended Hückel theory.

In proximity of the transition state angles θ and ϕ should be *ca.* 120 and 180° for α -attack, and 180 and 120° for β -attack respectively. The carbon-halogen distance should lengthen as the sulphur atom approaches. It should be noticed that the values for the $\text{R}-\text{C}\beta$ and the $\text{C}\alpha-\text{C}\beta$ bond lengths have been chosen as more appropriate for sp^2 than for sp hybridized carbon atoms.

The very crude approximations prevent any estimate of the absolute values of the activation energies. A qualitative picture of the trends should however be obtainable by comparison of the results for the various halogens and the various substituents, all other parameters being constant.

Choice of Extended Hückel Parameters.—Table 1 collects all needed parameters. For fluorine, no minimum was found for the energy as a function of the $\text{C}\alpha-\text{F}$

TABLE I

Extended Hückel parameters			
	Slater exponent	α_{2s} (eV)	α_{2p} (eV)
C	1.625 ^a	-21.4 ^b	-11.4 ^b
H	1.0 ^a	-13.6 ^b	
S	1.817 ^a	-20.0 ^c	-13.2 ^c
F	2.6 ^a	-34.5 ^d	-12.96 ^d
Cl	2.033 ^e	-25.29 ^f	-13.99 ^f
Br	2.054 ^e	-24.05 ^e	-12.52 ^e
I	1.9 ^e	-18.0 ^e	-11.4 ^e

^a R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248. ^b Ref. 9. ^c R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, 1970, **19**, 113. ^d Optimized values (see text). ^e E. Heilbronner, K. A. Muszkat, and J. Schäublin, *Helv. Chim. Acta*, 1971, **54**, 58. ^f K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, 1969, **14**, 206.

bond length in $\text{MeC}\equiv\text{CF}$, if ionization potentials¹¹ were used for α_{2s} and α_{2p} . Starting from these values these parameters were optimized, keeping the difference $\alpha_{2s} - \alpha_{2p}$ constant, to give a minimum energy corresponding to a reasonable value for the $\text{C}\alpha-\text{F}$ bond length. The value obtained (1.9 Å) cannot however be considered satisfactory.

Preliminary Calculations.—Table 2 collects observed and calculated structural data for a number of halogen- and sulphur-containing molecules. Figure 2 shows the energy curves as a function of carbon-halogen bond length in halogenomethanes, and methyl- and phenyl-halogenoacetylenes. The largest discrepancies between the observed and calculated values are, as expected, for fluorine-containing molecules. Another parameter of interest is the angle γ formed by the direction of the S-H bond in the thiolate anion and the direction of the triple bond (see Figure 1). For simplicity, it was decided to keep this angle constant rather than the C-S-H angle.

⁹ R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

¹⁰ R. Hoffmann, C. C. Wan, and V. Neagu, *Mol. Phys.*, 1970, **19**, 113; R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 1475; R. Hoffmann, R. Gleiter, and F. B. Mallory, *ibid.*, 1970, **92**, 1460; R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, p. 7091; R. C. Dobson, D. M. Hayes, and R. Hoffmann, *ibid.*, 1971, **93**, 6188; R. Hoffmann and W. D. Stohrer, *ibid.*, p. 6941; W. D. Stohrer and R. Hoffmann, *ibid.*, 1972, **94**, 1661; R. Hoffmann, J. M. Howell, and E. L. Muettterties, *ibid.*, p. 3047.

¹¹ J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S136.

Figure 3 shows the effects of systematic variations of γ for various positions of the sulphur atom with respect to the α -carbon atom of chloro(methyl)acetylene. Obviously, the large effect observed near the carbon atom [Figure 3(a)] decreases substantially, and almost

TABLE 2
Bond lengths (Å)

	C-X or C-S		C≡C	C-C
	Obs.	Calc.		
MeF	1.385 ^a	1.9		
MeCl	1.781 ^b	2.2		
MeBr	1.939 ^b	2.4		
MeI	2.139 ^b	2.65		
MeC≡CF	1.239 ^c	1.85		
MeC≡CCl	1.637 ^d	1.75		
MeC≡CBr	1.793 ^d	1.95	1.21 ^e	1.46 ^e
MeC≡CI	1.991 ^d	2.10	1.21 ^e	1.46 ^e
PhC≡CF		1.90		
PhC≡CCl		1.75		
PhC≡CBr		1.85		
PhC≡CI		2.00		
MeC≡CSH		1.60		
MeSH	1.82 ^a	2.2		

Missing values for the observed C_{α} -X distances in halogeno(phenyl)acetylenes have been replaced by the corresponding ones for halogeno(methyl)acetylenes.

^a 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' ed. L. E. Sutton, Chemical Society Special Publication No. 11, London, 1956. ^b S. L. Miller, L. C. Aamodt, G. Dousmanis, and C. H. Townes, *J. Chem. Phys.*, 1952, **20**, 1112. ^c Value obtained by subtracting from the C-F bond length in MeF the average decrease in bond length on going from chloro-, bromo-, and iodo-methane to the corresponding halogenoacetylene. ^d J. L. Duncan, *Spectrochim. Acta*, 1964, **20**, 1197. ^e J. Sheridan and W. Gordy, *J. Chem. Phys.*, 1952, **20**, 735.

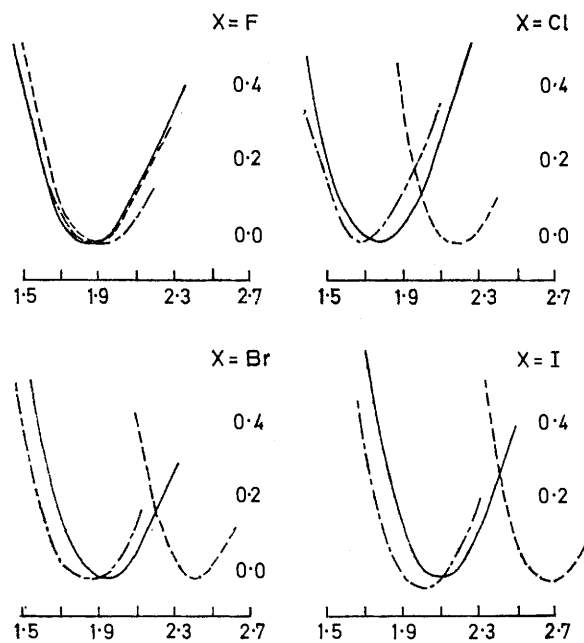


FIGURE 2 Energy curves (eV) as a function of C-X distance (Å): — halogeno(methyl)acetylenes; ---- halogenomethanes; - · - · - halogeno(phenyl)acetylenes

vanishes, as the C_{α} -S distance increases [Figures 3(b)–(d)]. Moreover, the effect should be the same in all

molecules, so that comparisons should not be too much affected by the particular choice of γ within a reasonable range. We used $\gamma = 10^\circ$ for α -attack and $\gamma = 170^\circ$ for β -attack.

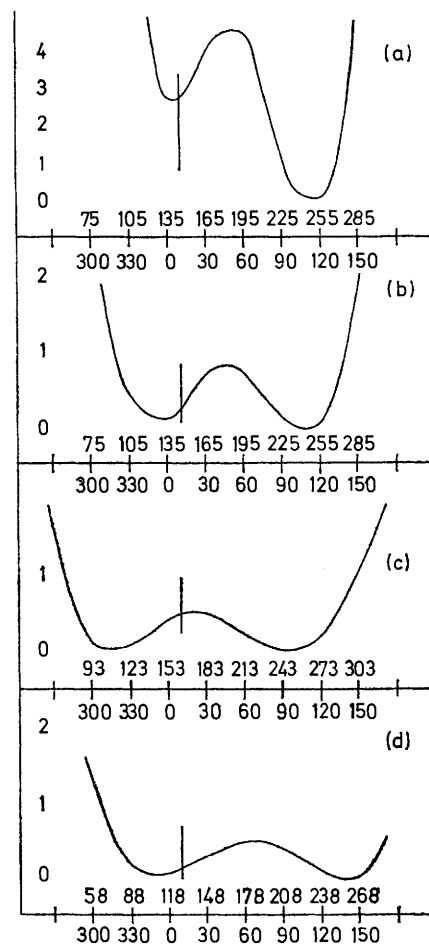


FIGURE 3 Energy curves (eV) as a function of γ (lower abscissa scales) and sulphur atom co-ordinates, x_S and y_S (Å): (a) $x_S = 0.5$, $y_S = -0.5$; (b) $x_S = 1.0$, $y_S = -1.0$; (c) $x_S = 2.0$, $y_S = -1.0$; (d) $x_S = 1.0$, $y_S = -2.0$. Upper abscissa scales refer to CSH. A vertical bar indicates the value of γ used for α -attack

RESULTS AND DISCUSSION

Figures 4–9 show the potential surfaces or energy curves obtained by moving the HS^- anion in the xy plane. All energy values are in eV and the zero reference is, in each case, the sum of the energies of the reactants $RC\equiv CX$ and of the ion HS^- . The structure of the reactants is summarized in Table 2; the bond lengths C_{α} - C_{β} and R - C_{β} observed for bromo- and iodo(methyl)acetylene were found to be independent of the halogen atom, and were used for the remaining halogeno(methyl)acetylenes and for the corresponding phenyl derivatives. For the C_{α} -X distance of each acetylene, two values were considered, the calculated and the experimental. The latter was used in the case of β -attack, while the calculated value was used in the case of α -attack and attack on the halogen atom.

In Figures 4—7 results refer to θ or $\phi = 120^\circ$, the most favourable values for the approach of the nucleophile.

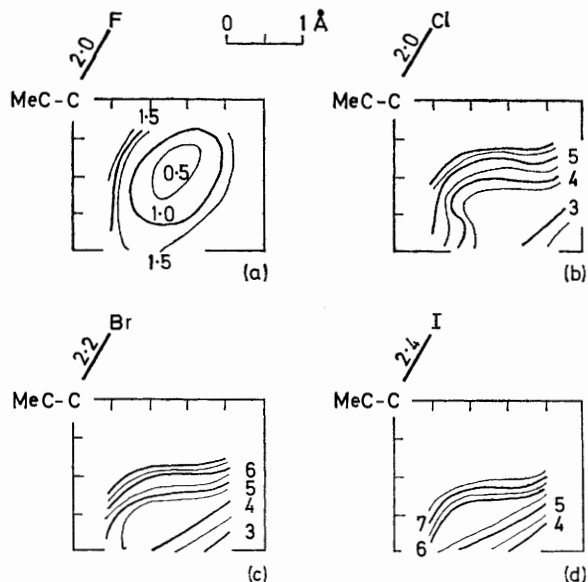


FIGURE 4 Halogeno(methyl)acetylenes: α -attack. Energy curves (eV) are drawn at intervals of 0.5 eV, $C_\beta\hat{C}_\alpha X 120^\circ$

(i) *Halogeno(methyl)acetylenes: α -Attack.*—Figure 4 shows the potential energy surfaces. A definite minimum, corresponding to an intermediate anion, was found in the case of the fluoro-compound. For the remaining halogens, a marked ripple, corresponding in each case to a reasonable geometry for a hypothetical intermediate anion, was found. From the size of the ripple and the

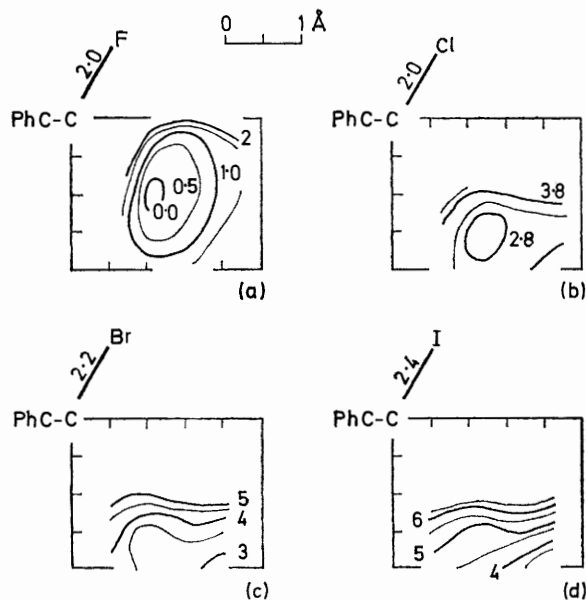


FIGURE 5 Halogeno(phenyl)acetylenes: α -attack. See caption to Figure 4

slope of the surface it can be envisaged that an intermediate is likely to be present in the case of $X = \text{Cl}$.

The probability decreases on going to bromine and even more so for iodine. It should be noticed that the reaction hypersurface has been sampled at intervals of 0.5 Å in x and y and for $\theta = 90, 120$, and 135° only, so that a shallow minimum is likely to have been missed.

(ii) *Halogeno(phenyl)acetylenes: α -Attack.*—For details of the assumed geometry of the benzene ring see Figure 1. The phenyl ring was considered to lie in a plane perpendicular to the plane containing the thiolate anion. Calculations showed that this situation is favoured over the one in which the thiolate ion and the phenyl ring are coplanar.

The reaction surfaces (Figure 5) are quite analogous to those for the methyl derivatives, and display the same trends. A definite minimum is obtained for fluoro- and chloro-(phenyl)acetylene; a minimum is very likely for $X = \text{Br}$.

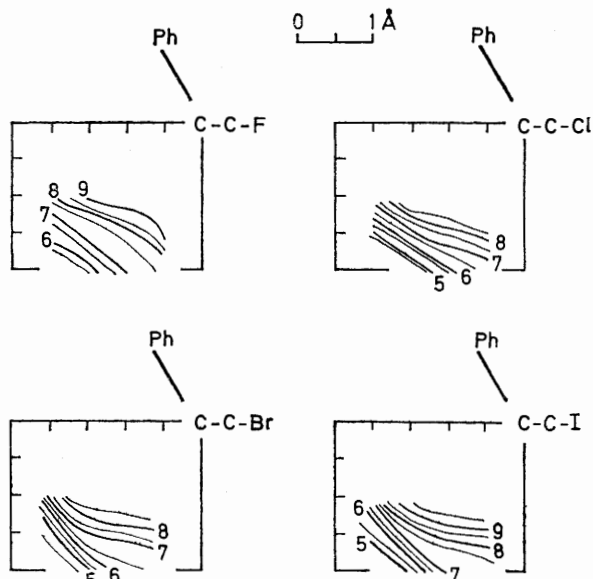


FIGURE 6 Halogeno(methyl)acetylenes: β -attack. Energy curves (eV) are drawn at intervals of 0.5 eV. Observed values for the $C_\alpha-X$ distance (Table 2) have been used throughout. $R\hat{C}_\beta C_\alpha 120^\circ$

(iii) *Halogeno-(methyl)- and -(phenyl)-acetylenes: β -Attack.*—Figures 6 and 7 show the surfaces obtained for β -attack on methyl- and phenyl-substituted derivatives, respectively. No minima were obtained, and only very small ripples appear. By the same criteria used in analysing the results of Figures 4 and 5 the formation of an intermediate is unlikely in all cases.

In the calculations presented in Figures 6 and 7 we used the experimental $C_\alpha-X$ distances. However, we found that energy surfaces were substantially independent of this distance, as can be seen from the example shown in Figure 8 for iodo(methyl)acetylene.

(iv) *Attack on the Halogen Atom.*—Figure 9 reports energy curves as a function of $C_\alpha-X$ and $X-S$ distances for a few interesting cases, the attack being considered to take place along the x axis, with $\gamma = 0^\circ$ (see Figure 1).

In the case of iodo(phenyl)acetylene a minimum is obtained for C_{α} -I distances $>2.5 \text{ \AA}$, strongly suggesting

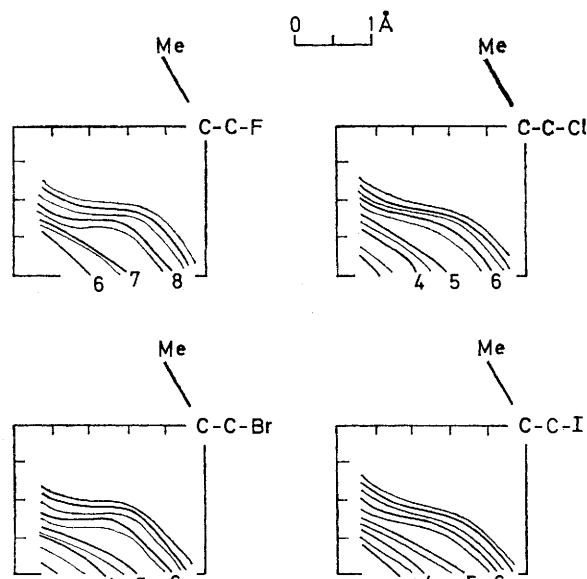


FIGURE 7 Halogeno(phenyl)acetylenes: β -attack. See caption to Figure 6

a possible $[RCC^- ISH]$ intermediate. Analogous behaviour was found for bromo(phenyl)acetylene. No minima were observed for other halogeno-(methyl)- or -(phenyl)-acetylenes for reasonable X-S distances.

(v) *Charge Distributions in the Intermediates.*—Figure 10 shows charge distributions from Mulliken's population analysis,¹² for the intermediates which have been found. In Figure 10(a)–(c) the intermediate structures correspond to the minima shown in Figures 4(a) and 5(a) and (b). In Figure 10(d) and (e) the structures are those of the minima on the lower curves in Figure 9(b) and (c).

Owing to the limited number of geometries considered for the reacting system, only the region of the potential

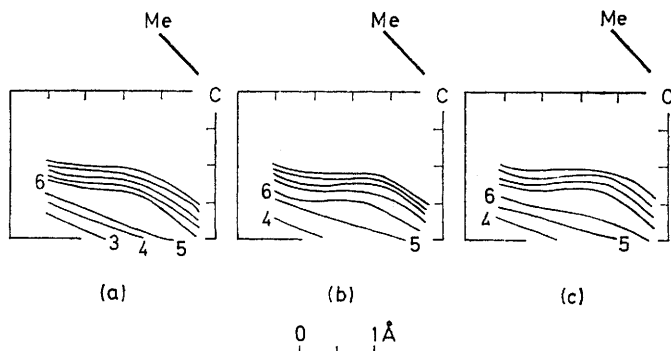


FIGURE 8 Iodo(methyl)acetylene: β -attack. Energy curves are drawn at intervals of 1.0 eV. $RC_{\beta}C_{\alpha} 135^{\circ}$; C_{α} -I (a), 2.2 Å; (b) 2.6 Å; (c), 2.8 Å

energy hypersurface where a possible intermediate could be found has been explored for each case. Therefore complete energy profiles along the reaction path are not available and no discussion of reactivity is possible

in terms of activation energies. Instead, relative reactivities can be judged on the basis of probability and stability of intermediates, by assuming these to be very similar in structure and relative energy to the corresponding transition states. In the case of nucleophilic attack on the α -carbon atom, a definite order of reactivity with respect to the leaving group was found both for aryl and alkyl substrates, namely $F > Cl > Br > I$. For each halogen the phenyl derivative is more reactive than the corresponding methyl derivative.

These relevant features are absent in the case of β -attack, where only slight differences appear on changing the nature of the substituent and/or the halogen. As a result, α -attack is consistently favoured over β -attack, with the possible exception of the iodo-derivatives, for which there is no clear prediction of reaction through α - or β -attack. When attack on the halogen atom was

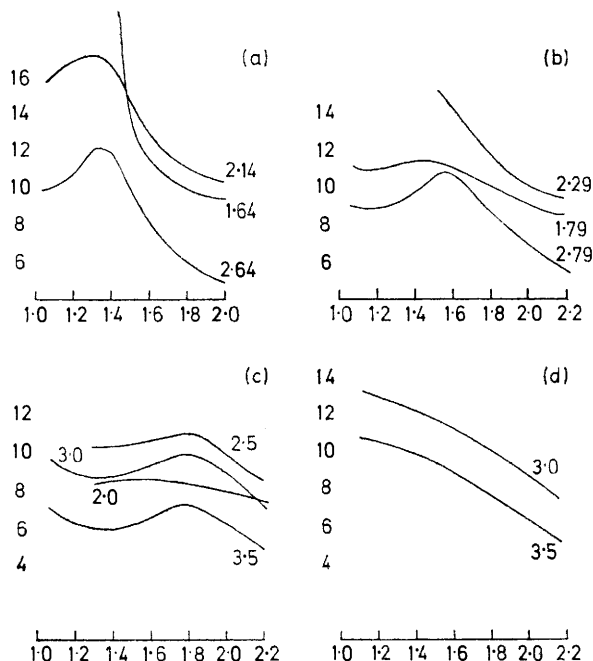


FIGURE 9 Energy curves (eV) for attack on the halogen atom: (a) chloro(phenyl)acetylene; (b) bromo(phenyl)acetylene; (c) iodo(phenyl)acetylene; (d) iodo(methyl)acetylene. Abscissa scales refer to the S-X distance, numbers near each curve to the C_{α} -X distance

considered, evidence of reactivity was found for iodo- and bromo-(phenyl)acetylene only; no alkyl derivative was found to be reactive through the attack on the halogen atom, not even in the case of the iodo-compound.

To compare these results with the outcome of experiments, it is important to remember that the calculations refer to isolated systems, while experiments are usually carried out in solution. However, general agreement is found.

Fluoroacetylene is attacked on the α -carbon atom by thiols: ^{4a} while the reaction ends up as an addition instead of a displacement, the result is significant for

¹² R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.

both types of reaction, and is in agreement with the high reactivity of sulphur nucleophiles towards the α -carbon atoms of fluoroacetylenes resulting from our calculations.

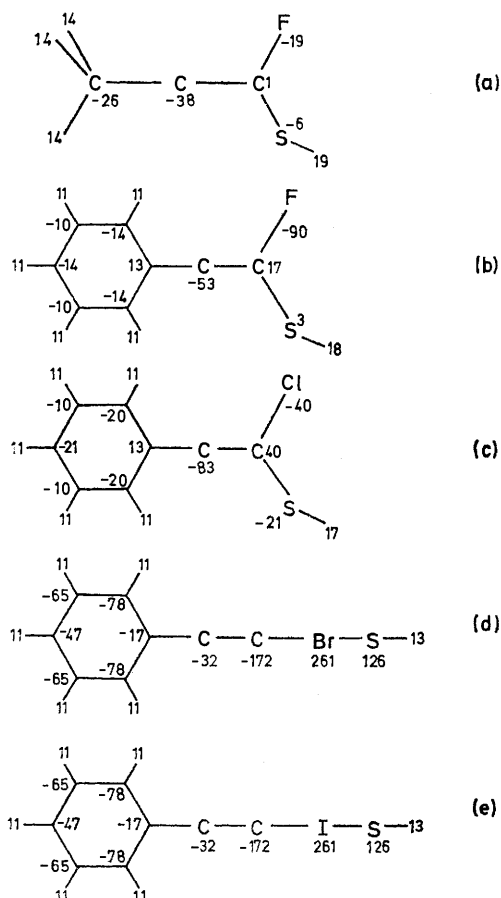


FIGURE 10 Charge distributions for the intermediates (see text)

Addition of thiolates to chloroacetylene is to the β -carbon atom; for alkylchloroacetylenes also nucleo-

philic attack occurs at the same position, α to the alkyl group.^{4a} The idea of mechanism (c) for substitution was born out of this observation.³ Arylchloroacetylenes were found to give the corresponding sulphides by substitution with thiolates in dimethylformamide;^{1,8b} kinetic evidence (leaving-group effect, Hammett correlation of the effect of ring substituents) favours attack at the α -carbon atom, as do the present calculations. The same mechanism has been proposed for the reaction with some nucleophiles including HS⁻, in protic solvents.^{8a} On the other hand, in these solvents other sulphur nucleophiles were found to attack the chlorine concurrently with the α -carbon atom.^{8a}

In the case of bromoacetylenes, a greater tendency towards halogen attack has been recognized, both for alkyl^{4b} and aryl^{8a} derivatives. In the latter case, mechanism (b) for the reaction in protic solvents is supported by the nature of the products and by the kinetics. However, mechanism (a) was found for the reaction of arylbromoacetylenes with toluene-*p*-thiolate in dimethylformamide.^{8b} Both mechanisms are possible according to the present calculations.

Available evidence for alkyl-^{4a} and aryl-iodoacetylenes^{8a} indicates attack at iodine by thiolates and/or other nucleophiles. It can be noted that for halogen attack computations predict the order of reactivity as I > Br > Cl.

The charge distributions shown in Figure 10 can be used only for comparison since it is well known that the atomic charges computed by extended HMO are too large. Anyway they correspond qualitatively to what might have been expected for reaction intermediates. The strong charge separations in Figure 10(d) and (e) confirm that the influence of protic solvents determines the mechanism of halogen attack.⁸

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