Figure 2. Proton n.m.r. spectrum of a solution of water in liquid ammonia buffered with cyclopentadiene and its anion.

spectrum of a solution of 0.86 M water in liquid ammonia saturated with sodium hydroxide is shown in Figure 1. The peak at −4.32 p.p.m. from external tetramethylsilane, corresponding to the water protons, is broadened because of exchange with hydroxide. The solvent signal is a sharp triplet, indicating that the ammonia is not taking part in the exchange process to any appreciable extent. A solution 6 M in water and 0.02 M in sodium hydroxide gives a partially collapsed ammonia triplet.

Figure 2 shows the n.m.r. spectrum of a solution of water in ammonia buffered with cyclopentadiene and its anion. The peaks at −6.43 and −2.91 p.p.m. are due to cyclopentadiene, that at −5.56 p.p.m. is due to the cyclopentadienide ion, and the sharp resonance at −4.32 p.p.m. is due to water. No precipitation of sodium hydroxide is observed. These observations indicate that water is a weaker acid than cyclopentadiene and that it does not exchange rapidly with ammonia. Ogg[5] has suggested a rate constant of approximately 4.6×10^8 l. mole^{-1} sec.$^{-1}$ for the reaction

$$H_2O + NH_3 = OH^- + NH_4^+$$
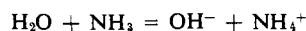
but a rate constant closer to that found for the analogous reaction of ethyl alcohol with ammonia (0.0303 sec.$^{-1}$) would seem more appropriate.[6] The exchange of water in unbuffered liquid ammonia solutions may be explained by a mechanism involving ammonium ion

$$NH_4^+ + \overset{H}{\overset{|}{O}}-H + NH_3 \rightleftharpoons NH_3 + H-\overset{H}{\overset{|}{O}} + NH_4^+$$
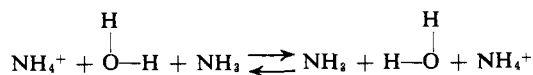
A similar mechanism has been shown to operate in aqueous solutions of ammonium ion.[7]

(5) R. A. Ogg, Discussions Faraday Soc., 17, 215 (1954).
(6) W. L. Jolly and C. J. Hallada, in "Non-aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965.
(7) S. Meiboom, A. Loewenstein, and S. Alexander, J. Chem. Phys., 29, 969 (1958).

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Reaction of Thermal Carbon Atoms in Solids. Relation to Properties of Vapor-Deposited Carbon

Sir:

In recent years extensive investigations have been made of the properties of free carbon atoms[1] in the form of C^{11} (20 min.) as produced by nuclear reaction. With hydrocarbons the most common primary reactions have been shown to be addition to the C—H and C=C bonds.[2] The resulting adducts undergo secondary processes, the nature of which depend on (1) the internal excitation and spin state of the adduct[2] and (2) the character and phase of the surrounding molecules.[2,3]

The effect of the first factor has been investigated making use of the fact that C^{11}, as produced by nuclear recoil, has excess kinetic energy. It has been shown that in pure hydrocarbons carbon atoms will usually react while still moderately "hot."[2,4,5] The adducts formed are therefore highly excited and unless rapidly deactivated by collision are likely to undergo extensive decomposition. Thus the reaction of recoil C^{11} with pure gaseous hydrocarbons usually leads to a large yield of acetylene.[6] On the other hand, if the carbon atoms are thermalized prior to reaction by diluting the system with a large excess of inert noble gas moderator, the adducts are less excited and less likely to fragment to form products such as acetylene. (However, they are still sufficiently excited by the energy released on binding the carbon atom that in excess neon, a poor deactivator, there is still substantial acetylene yield.) This competition is shown in outline form in Figure 1.
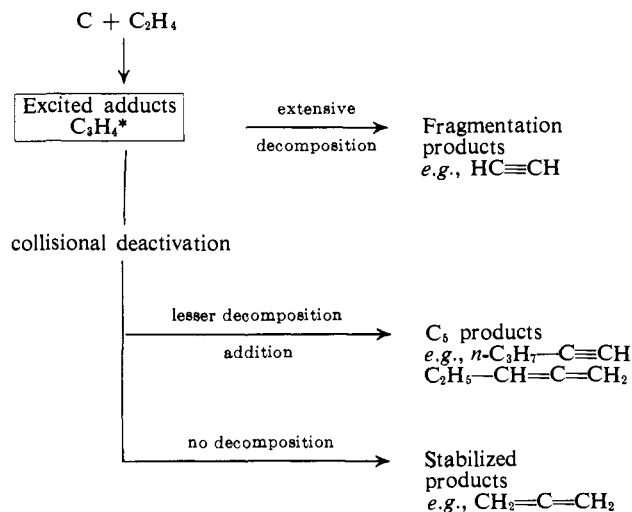

Figure 1. Outline of competing modes of reaction of adducts formed by carbon atom insertion into C—H and C=C bonds (see ref. 2).

(1) For recent reviews see A. P. Wolf, Advan. Phys. Org. Chem., 2, 201 (1964); R. L. Wolfgang, Progr. Reaction Kinetics, in press; C. MacKay and R. Wolfgang, Science, 148, 899 (1965).
(2) (a) M. Marshall, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc., 86, 4741 (1964); (b) J. Dubrin, C. MacKay, and R. Wolfgang, ibid., 86, 4747 (1964).
(3) G. Stocklin and A. P. Wolf, ibid., 85, 229 (1963).
(4) C. MacKay, P. Polak, H. E. Rosenberg, and R. Wolfgang, ibid., 84, 308 (1962).
(5) J. Dubrin, H. E. Rosenberg, R. Wolfgang, and C. MacKay, Proceedings of the Symposium on Chemical Effects Associated with Nuclear Reactions, I.A.E.A., Vienna, 1964.
(6) C. MacKay and R. Wolfgang, J. Am. Chem. Soc., 84, 2399 (1962).

The effect of the second factor is apparent on comparing hot carbon atom reactions in condensed and gaseous systems. Again the probability of fragmentation is reduced: in this case because collisional deactivation of the adduct is enhanced.[2,3]

To this time, however, no experiments on the reaction of thermalized C^{11} in solid media have been made. The model of carbon atom reactions[2] predicts that, under these circumstances, the combination of thermalization of the reacting atoms and rapid deexcitation of the adducts should further reduce the yield of fragmentation products while enhancing other yields.

In this communication we report on the reactions of recoil C^{11} with ethylene embedded in solid xenon matrices produced by rapidly freezing down gaseous mixtures at $-196°$. C^{11} produced by nuclear reaction of the C^{12} beam of the Yale heavy ion accelerator was allowed to recoil into the mixture. This technique and the radiogas-chromatographic method of analysis have been described previously.[7]

Results are given in Table I. This shows major yields and also a ratio acetylene: $(C_3 + C_5$ products), which measures the probability of major fragmentation of the primary adducts. The effect of thermalization of the carbon atoms[8] on dilution of ethylene gas by Xe moderator is apparent (column 3). The effect of increased collisional deactivation of the primary adduct appears on freezing the ethylene (column 4). The combined influence of both factors is shown by the experiments on ethylene in solid xenon (column 5). Here acetylene becomes a minor product.

Table I. Some Major Products of Carbon Atom Reaction with Ethylene[a]

Product	C_2H_4 gas[b]	1%C_2H_4– 99%Xe gas[b]	C_2H_4 solid[c]	1%C_2H_4– 99%Xe solid[c]
Acetylene	38.5	24.8	19.5	6.5
Allene	16.5	4.8	11.2	26.3
Methylacetylene	4.5	1.5	4.0	3.5
Pentyne-1	6.6	20.2	7.5	11.2
Ethylallene	3.3	7.1	6.5	8.6
Spiropentane	<0.5	<1.5	<0.5	<1.5
Ratio acetylene/ (C-3 + C-5 products)	1.25	0.74	0.67	0.13

[a] Values given in % of total volatile activity.   [b] 25°, 76 cm.   [c] Solid, at $-196°$.

These results, in bearing out the predictions of the model, strikingly support its essential validity. They also provide new information on mechanistic details, which will be fully discussed in a later paper.[9]

The present data are closely relevant to recent work of Skell and Engel, and Sprung, Winstein, and Libby, on

the reaction of carbon vapors deposited on surfaces.[10,11] Results of these studies have been interpreted on the basis that carbon atoms are among the reactive species involved.[10,11] Such a hypothesis is supported by identification of products[10] which appear to be formed by the double bond addition mechanism previously established as an important mode of carbon atom reaction.[2,4]

Skell and Engel found a number of differences between their results and the earlier findings on free carbon atoms. In particular they failed to find acetylene as a product. This difference should not occasion surprise, however, being not only plausible but in the direction predicted by the reaction model[2] postulated earlier. The present work, indicating that the acetylene yield diminishes sharply as the carbon atoms are thermalized and the adducts are efficiently de-excited, confirms that there is indeed no discrepancy.

The finding by Skell and Engel that deposited carbon vapor forms spiropentanes on reaction with butenes does contrast with our results (Table I), which show that spiropentanes are not produced in significant yield by reaction of thermalized free carbon atoms in xenon–ethylene matrices. This could indicate that Skell and Engel are dealing with the reaction of carbon atoms complexed by surface material rather than with free carbon atoms. However, this is not necessarily the case. As has been pointed out (see footnotes 21 and 22 of ref. 2a), the intermediate formed by carbon atom addition to a double bond in a small molecule (e.g., ethylene) is likely to collapse to an allene while a similar adduct with a larger system (e.g., butene) may survive to react with a second molecule to form spiropentanes.

Taking into account the nature of the reagent molecules and their state of condensation the results on surface-deposited carbon do indeed follow naturally from earlier findings on free carbon reactions. Nevertheless, some differences may be expected in view of the very different experimental conditions. This is particularly true if the vapor-deposited carbon atoms do not immediately react with the surface itself. Thus Skell and Engel observed a change in product distribution on delaying addition of reagent to carbon vapor which had been deposited on an apparently inert surface. Their interpretation, that this was due to electronic decay of ^1D and ^1S atoms to the ^3P ground state, is plausible and consistent with information on triplet and singlet methylenes. However, it is known that modification and complexing of reactive species at surfaces commonly occurs, particularly if an ultrahigh vacuum (of the order of 10^{-10} torr) is not maintained.[12] Although the complexes formed in this case could still add carbon atoms to subsequently added reagent, the resulting products may differ from those of free carbon atoms. A time-dependent behavior of the product spectrum would then result. Detailed information on experimental conditions may resolve such ambiguities and permit a closer assessment of the degree of similarity in the properties of surface-deposited and free carbon atoms.

(7) J. Dubrin, M. Pandow, C. MacKay, and R. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

(8) Comparison with Ne moderator data[2,4,5] shows that Xe is, as expected, a less effective moderator. At the mole fractions used it appears that thermalization is not complete and there is still some contribution from hot reaction.

(9) We do not discuss here the interesting questions (1) of whether the carbon atom reacts immediately or is trapped and does not react until the matrix is destroyed by warming prior to analysis; (2) of whether the ethylene is present as microcrystals or as a solid solution. These matters do not bear on the primary conclusion reached here.

(10) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(11) J. Sprung, S. Winstein, and W. F. Libby, *ibid.*, **87**, 1812 (1965).

(12) See, *e.g.*, R. W. Roberts, *J. Phys. Chem.*, **66**, 1742 (1962).

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Legate Ions. The Use of the Oxibase Scale to Predict Leaving Group Orders from Carbon in S_N2 Reactions[1]

Sir:

A fundamental problem of structure–reactivity relationships has been that of the quantitative correlation of leaving group effects from saturated carbon atoms. It is generally stated that the less basic the substituent the more easily it is removed.[2] An empirical relationship has been suggested by Swain and Lohmann[3] using the reaction of methoxide with methyl–X derivatives in methanol at 25°.
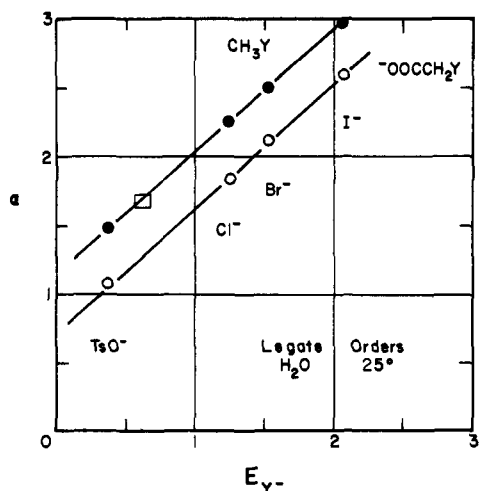

Figure 1. Plot of α vs. the electrode constant E of the leaving group, Y, in water at 25° for a series of alkyl substrates having legate anions of strong acids. Data from ref. 11. □ represents the value of α obtained from the rate data with trimethyl phosphate; the E value of the leaving group, dimethyl phosphate monoanion, can then be estimated.

We wish to suggest that a leaving group is a nucleophile regressing or leaving the reaction center rather than approaching the electrophilic center. The leaving group then can be correlated with nucleophilic constants of oxidation and basicity.

Foss[4] first suggested the use of oxidation potentials to predict reactivity of various nucleophiles in S_N2 reactions. Edwards[5] then made the quantitative cor-

relation (3) between the *oxi*dative dimerization (6) and its *basicity* toward a proton (5)

$$X^- + CH_2Y \xrightarrow{k} CH_3X + Y^- \tag{1}$$

$$H_2O + CH_3Y \xrightarrow{k_0} CH_4OH + Y^- + H^+ \tag{2}$$

with

$$\log k/k_0 = \alpha E + \beta H \tag{3a}$$

or

$$\frac{\log k/k_0}{E} = \alpha + \beta \left[\frac{H}{E}\right] \tag{3b}$$

$$E = \epsilon_{X^-} + 2.60 \text{ v.} \tag{4}$$

$$H = pK_{aX^-} + 1.74 \tag{5}$$

$$2X^- \xrightleftharpoons{\epsilon_{X^-}} X_2 + 2e^- \tag{6}$$

all in water at 25.0°. We wish to suggest that eq. 3 be called the *oxibase scale*.

In keeping with the symmetry of the two model systems used to define (3), we wish to suggest that α is a *reduction term* and β is an *acidity term* of the substrate. By the rigorous application of nonequilibrium thermodynamics to (1) and (2), it can be shown that α for carbon substrates ought be linearly related to the electrode potential of the legate ion,[6] Y^-, of *strong acids*. Thus leaving group orders ought to be correlated with the same model systems used to correlate the nucleophiles in water at 25°. The data (all in H_2O at 25°) are presented[7] in Figure 1. The slopes are unity as predicted by theory.

The β of the alkyl substrate is claimed to be an acidity term which is a measure of the amount of partial charge on the carbon. Application of a *free energy cycle*[8] shows that β is related to the square of the electronegativity difference between the legate ion and the carbon. In more simple terms, the more positive the carbon the more positive is β. The values of β and α have been computed by multiple regression analysis using the experimental data of ref. 11.

C–I	β	−0.0134
C–Br		+0.002
C–Cl		+0.008
C–OTs		+0.013
more positive C		more positive β

Application of the data presented in Figure 1 allows estimation of nucleophilic constants E for very poor

(1) Paper VI on Displacement Reactions. Paper V: R. E. Davis and A. Cohen, *J. Am. Chem. Soc.*, **86**, 440 (1964). A qualitative use of the oxibase scale to predict which group will leave in a complex reaction is discussed in this paper.
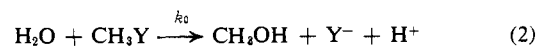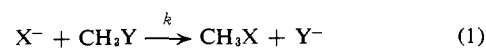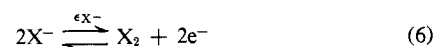
(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 258–263.

(3) C. G. Swain and K. H. Lohmann, unpublished data reported by E. R. Thornton in "Solvolysis Mechanisms," The Ronald Press, New York, N. Y., 1964, pp. 163–166.

(4) O. Foss, *Acta Chem. Scand.*, **1**, 8, 307 (1947).

(5) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1889 (1956); J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(6) Derived from *legare*, to send out.

(7) Bunnett (J. F. Bunnett, *J. Am. Chem. Soc.*, **79**, 5969 (1957)) in this interesting paper uses Edwards' polarizability, P, to estimate E. Then β was assumed equal to zero and a test made of

$$\log \left[\frac{k_{C_2H_5I}}{k_{C_2H_5Br}}\right]_{X^-} = (\alpha_{C_2H_5I} - \alpha_{C_2H_5Br}) P_{X^-} + \log \left[\frac{k_{C_2H_5I}}{k_{C_2H_5Br}}\right]_{H_2O}$$

This equation or one like it derived from (5) tests the validity of the constancy of α and the nucleophilic parameter, P, of the nucleophile. It does not relate α to the legate potential. In a following paper in this series the use of P will be discussed. Unfortunately kinetic data have not been always measured in the same solvent as that used to calculate P. Bunnett tested his equation with rate data obtained in acetone using P values determined in water.

(8) D. H. McDaniel and A. Yingst, *ibid.*, **86**, 1334 (1964). These authors report an interesting thermodynamic cycle and have used the *enthalpies* to derive group electronegativities. The present work has used the *free energies* of the McDaniel cycles since the application of statistical mechanics can allow one to compute the necessary terms.