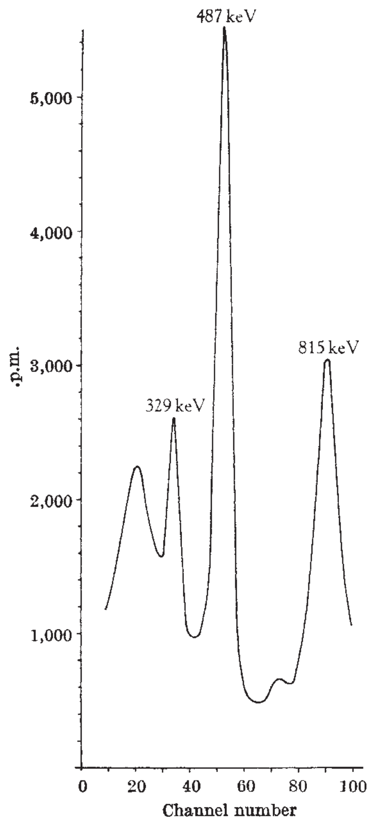

Fig. 1. γ-Coincidences with 1,596-keV line of lanthanum-140

This seems to prove that debris from the Sinkiang explosion reached Copenhagen by transportation in the upper troposphere in less than 10 days.

Later measurements on a rain sample from October 23 finally proved that the transportation time did not exceed 7 days.

J. J. LED
L. KRISTENSEN

Danish Defence Research Board,
Copenhagen.

CHEMISTRY

Chemical Behaviour of Difluorocarbene, and the Dissociation of the Carbon—Carbon Bond in Tetra-fluoroethylene

Bond strengths. The heat of formation of CF_2 has been estimated through electron impact, thermochemical and kinetic studies. The most recent measurements were obtained through a study of the pyrolysis of CF_2HCl at 530°–750° C, which is believed[1–3] to follow the mechanism:

$$CF_2HCl \rightleftharpoons CF_2 + HCl$$
$$CF_2 + CF_2 \rightleftharpoons C_2F_4$$

Either by interpolation from known data, or by assuming the heat of formation of C_2F_4 (–151·5 kcal/mole (ref. 4)) and combining this with the thermodynamic data for the equilibrium:

$$2CF_2HCl \rightleftharpoons C_2F_4 + 2HCl$$

it is possible to estimate the heat of formation of CF_2HCl (~ -112 kcal/mole); an estimate of the Arrhenius factors of the elementary steps can be derived from the kinetic analysis. Combination of the thermochemical and kinetic data yields $\Delta H_f(CF_2) \lesssim -40$ kcal/mole, and hence $D(F_2C–CF_2) \lesssim 70$ kcal/mole. Similar conclusions have been reached by Stull[5], on the basis of a study of the formation of C_2F_4 from carbon and CF_4 in a furnace[6]. Majer and Patrick[7] have suggested that higher (less negative) values for $\Delta H_f(CF_2)$, which have been reported on the basis of electron impact studies, result from the production of excited fragments in the primary dissociation.

Whatever may be the absolute value of the heat of formation of CF_2, there is little doubt that it leads to a very low value for $D(F_2C—CF_2)$, probably ~ 70 kcal/mole, and this conclusion is consistent with other evidence to be presented. By contrast the heat of formation of CH_2, although not known with absolute certainty[8], leads to $D(H_2C—CH_2) \sim 150$ kcal/mole. However, the C—C bond stretching frequency in C_2H_4 is ~ 250 cm^{-1} lower than in C_2F_4 (refs. 9 and 10) and the C—C bond length is $\sim 0{\cdot}02$ Å longer. Despite the very low bond dissociation energy in C_2F_4, there is no doubt that, in the region of the potential minimum at least, the carbon atoms remain linked by a double bond.

Decomposition of fluoromethanes and olefines. The spectroscopic detection of CF_2 produced in the flash photolysis of many fluorinated methanes and olefines has been reported[11–13]. Evidence has been obtained, indicating that CF_2 is produced in a 'molecular' split, in the photolysis of CF_2HBr and CF_2Br_2 (and CF_3COOH); gas chromatographic and mass spectrometric analysis of the volatile products of flash photolysis of $CF_2 : CCl_2$ and $CF_2 : CFCl$ have revealed $CF_2 : CF_2$ and $CCl_2 : CCl_2$, and $CF_2 : CF_2$ and $CFCl : CFCl$ respectively[14]. The ready production of CF_2 from these olefines, and from C_2F_4, with light in the quartz ultra-violet, again emphasizes the ease of dissociation at the C—C bond in these molecules. The products of the Hg (6^3P_1) photosensitized decomposition of C_2F_4 have been interpreted in terms of a primary dissociation at the C—C bond[15]; this places $D(F_2C—CF_2) < 112$ kcal/mole.

The ultra-violet absorption spectrum of CF_2 that is observed after flash photolysis is that of its ground state, which is a singlet, $^1A_1$. Its decay is slow and the absorption persists for > 20 msec (ref. 12). Evidently, CF_2 ($^1A_1$) does not rapidly dimerize in the gas phase at room temperature. If CF_2 is produced from any of the molecules mentioned here, in an atmosphere of oxygen rather than nitrogen, its yield and decay are not sensibly altered; any homogeneous reaction of CF_2 in its ground electronic state with molecular oxygen cannot be detected at room temperature. Fielding and Pritchard could find no evidence for reaction between CF_2 and O_2, H_2, CO, C_2H_4 or C_3H_8 at 250° C (ref. 16). Kinetic data relating to reactions of CF_2 in the gas phase have been obtained, however, at 530°–750° C. It was found that the pyrolysis of CF_2HCl is inhibited by addition of HCl or HBr, and that in the latter case CF_2HBr is a product[2,3]. The activation energies for the reactions:

$$CF_2 + HCl \rightarrow CF_2HCl$$

and:

$$CF_2 + CF_2 \rightarrow C_2F_4$$

were estimated to be ~ 6 kcal/mole, though in the latter case the uncertainty in the estimate was greater than the estimate itself. However, it cannot be assumed that the dimerization of CF_2 requires no energy of activation, in view of the very slow decay of CF_2 after its production in flash photolysis. Of particular note are the Arrhenius factors for the dissociation of C_2F_4, which were found to be $10^{16 \cdot 7}$ sec^{-1} and 70 kcal/mole.

The slow decay of CF_2 ($^1A_1$), produced from C_2F_4, indicates that the initial approach of two CF_2 molecules in their ground singlet states is repulsive. Let us suppose, then, that near the minimum of its ground electronic state C_2F_4 is 'attempting' to dissociate into two CF_2 molecules in their lowest triplet state, $^3B_1$ (assumed to be non-linear by analogy with $SO_2(^3B_1)$, with which it is iso-electronic[17]). The initial approach of two triplet species would be

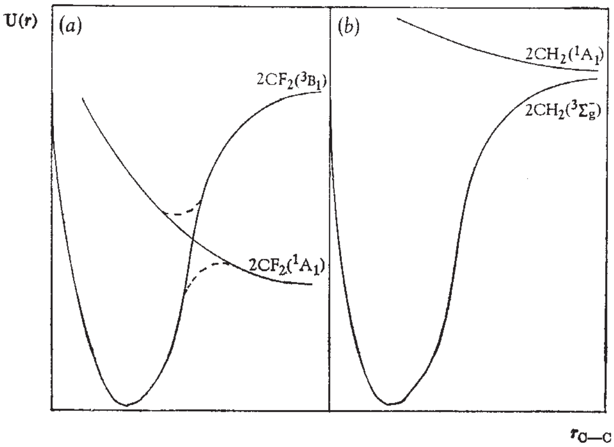

Fig. 1. Potential energy curves for C_2F_4 (*a*) and C_2H_4 (*b*)

attractive, and would be represented by a descending potential curve; it would cross the repulsive curve correlating with two normal CF_2 ($^1A_1$) molecules, since these will lie at a lower energy. The nett result is represented in Fig. 1*a*, where the potential energies are plotted as a function of the C—C separation (assuming that the remaining bond lengths and valence angles are 'frozen'). In C_2H_4, the products of dissociation at the C—C bond would be CH_2, which has a triplet ground state, $^3\Sigma_g^-$ (ref. 18). As in the case of CF_2 ($^3B_1$), these would approach each other along an attractive curve, but one which now cannot cross the curve correlating with $2CH_2$ ($^1A_1$), since this lies at higher energies (see Fig. 1*b*).

Some consequences of this interpretation can be listed: (i) The dissociation energy of the C—C bond in C_2F_4 will be reduced by an energy approximating to twice the energy of CF_2 ($^3B_1$) above its ground state. The depth of the perturbed curve representing the ground electronic state of C_2F_4 is $\sim$ 70 kcal/mole below its dissociation limit. Assuming that dissociation to two triplet carbenes requires $\sim$ 160 kcal/mole, as in C_2H_4, CF_2 ($^3B_1$) is estimated to lie $\sim$ 45 kcal/mole above CF_2 ($^1A_1$); (ii) the association of two singlet CF_2 molecules will require an activation energy the magnitude of which will depend on the height of the 'cross-over' point; (iii) the first excited singlet state of C_2F_4 will possess a relatively shallow minimum and a considerably increased equilibrium C—C distance. The longest wave-length ultra-violet absorption of C_2F_4 should be continuous on the basis of the Franck–Condon principle, and lead to dissociation at the C—C bond. In the event of predissociation the primary products would be singlet CF_2 molecules. The ultra-violet absorption is indeed continuous at wave-lengths around 2000 Å (ref. 19), and it is this transition which is excited in the flash photolysis of C_2F_4; (iv) the C—C stretching frequency in the ground state of C_2F_4 should show strong anharmonicity—this might be detected if high overtones could be observed in its infra-red spectrum. There is no conflict between the low dissociation energy of the C—C bond and its high stretching frequency, since the former relates to the behaviour of C_2F_4 at its dissociation limit, and the latter to its behaviour around the minimum, where it is unaffected by the perturbation occurring at higher energies; (v) the Arrhenius factors for the dissociation of C_2F_4 should reflect the perturbation of the ground state curve. The high-frequency factor ($10^{16\cdot7}$ sec^{-1}) is consistent with completely free rotation in the transition state (at the top of the maximum in the ground state curve), as has been proposed in the dissociation of N_2O_4.

It is of interest to extend the interpretation to the mixed ethylene $CF_2:CH_2$. In this case, one may expect the dissociation energy to be reduced by only half the amount in C_2F_4, since CH_2 has a triplet ground state. The difference between the dissociation energy of $CF_2:CH_2$ and $CF_2:CF_2$ should be the energy of CF_2 ($^3B_1$) above its ground state. The heat of formation of $CF_2:CH_2$ is $-77\cdot5$ kcal/mole[4], and taking $\Delta H_f(CF_2) \sim -40$ kcal/mole and $\Delta H_f(CH_2) \sim 86$ kcal/mole, $D(H_2C—CF_2) \sim 123$ kcal/mole. Subtracting $D(F_2C—CF_2)$ from this leaves $\sim$ 53 kcal/mole, which is reasonably close to the estimate of $\sim$ 45 kcal/mole for the excitation energy of CF_2 ($^3B_1$), considering the approximate values for the numerical data. Flash photolysis of $CH_2:CF_2$, using light of wave-length greater than 1700 Å, does indeed result in the transient appearance of CF_2 ultra-violet absorption bands, though with an intensity greatly reduced in comparison with C_2F_4, consistent with the greater energy required for dissociation.

I thank Prof. A. D. Walsh for his advice.

J. P. SIMONS

Department of Chemistry,
University of Birmingham.

[1] Hudlicky, M., *Chemistry of Organic Fluorine Compounds*, 268 (Pergamon Press, London, 1961).
[2] Gozzo, F., and Patrick, C. R., *Nature*, **202**, 80 (1964).
[3] Edwards, J. W., and Small, P. A., *Nature*, **202**, 1329 (1964).
[4] Neugebauer, G. A., and Margrave, J. L., *J. Phys. Chem.*, **60**, 1318 (1956).
[5] Stull, D. R., *JANAF Thermochemical Tables* (1961).
[6] Farlow, M. W., U.S. Patent, 2,709,192 (May 24, 1955).
[7] Majer, J. R., and Patrick, C. R., *Nature*, **201**, 1022 (1964).
[8] Frey, H. M., *Progress in Reaction Kinetics*, **2**, 131 (1964).
[9] Sheppard, N., and Simpson, D. M., *Quart. Rev.*, **6**, 1 (1952).
[10] Nielsen, J. D., Claasen, H., and Smith, A., *J. Chem. Phys.*, **18**, 812 (1950).
[11] Mann, D. E., and Thrush, B. A., *J. Chem. Phys.*, **33**, 1732 (1960).
[12] Simons, J. P., and Yarwood, A. J., *Nature*, **192**, 943 (1961).
[13] Majer, J. R., and Simons, J. P., *Advances in Photochemistry*, **2**, 137 (1964).
[14] Simons, J. P., Cadman, P., and Tatham, P. E. R. (unpublished work).
[15] Atkinson, B., *J. Chem. Soc.*, 2684 (1952).
[16] Fielding, W., and Pritchard, H. O., *J. Phys. Chem.*, **64**, 278 (1960).
[17] Merer, A. J., *Dis. Faraday Soc.*, **35**, 127 (1963).
[18] Herzberg, G., *Proc. Roy. Soc.*, A, **262**, 291 (1961).
[19] Walsh, A. D. (personal communication).

Nuclear Magnetic Resonance Standards for Aqueous Solutions

FOR the nuclear magnetic resonance investigation of interaction in solution, careful consideration must be given to the choice of standard against which changes in chemical shift are to be measured. An external standard is in many ways ideal, but a correction has then to be applied to the observed chemical shift, due to differences in bulk magnetic susceptibilities. The true chemical shift δ is given by the equation:

$$\delta = \Delta\nu + g(\chi_{ref} - \chi_{sol}) \quad (1)$$

where $+\Delta\nu$ is the observed upfield shift, in p.p.m., of a line with respect to the reference, and χ_{ref} and χ_{sol} the volume magnetic susceptibilities of the reference and solution being investigated. The value of g is determined by the shape of the interface of contact between the reference and the solution. Since it is somewhat tedious to measure susceptibilities[2], many investigators have either ignored any corrections (thereby invalidating the work[3]) or have used internal standards, for which no susceptibility corrections have to be applied.

We used dioxan[4] as an internal standard for an investigation of aqueous resorcinol solutions. It transpired that the effects due to resorcinol–dioxan interactions are much greater than the effect due to resorcinol–water interactions. This highlights the danger of using an internal standard. To avoid interactions involving the reference compound, external standards must be used. The required χ values can be determined by the nuclear magnetic resonance method using a stationary pair of coaxial cylindrical tubes[5]. In our hands these tubes proved difficult to make and those that were made had such a large geometrical asymmetry as to give results even less accurate than those previously reported[2].