are felt to be responsible for the increased rate at which it is converted thermally. These strains are undoubtedly much less than those which prevail during plastic deformation. As illustration of this fact it is pointed out that preliminary shearing enhances the rate of thermal conversion at 250° by a factor near 100 whereas the rate of conversion during plastic deformation is about 14 orders of magnitude faster than the estimated rate of thermal conversion at the temperature employed during shear.

This interpretation is consistent with a number of related facts. Cold worked metals require high temperatures and appreciable times for complete annealing. Heating a solid sample of sheared potassium hexacyanoferrate(III) for 1.5 hours at 315° induced only a partial recrystallization of the potassium hexacyanoferrate(II) as determined by the crystal sensitive bands in the infrared spectrum. The factor by which the rate of thermal decomposition of potassium hexacyanoferrate(III) is enhanced by preliminary shearing falls from 100 to 20 during the course of the thermal decomposition, a fact which is explained by thermal annealing of some of the residual shear strains. The mere presence of the products of decomposition of potassium hexacyanoferrate(III) does not accelerate its rate of thermal decomposition.[11]

As pressure is increased the rate of conversion with shear of potassium hexacyanoferrate(III) rises more rapidly than the shear stress rises (Fig. 2). With a pressure increase from 10,000 to 40,000 atm. for example, the rate of reaction increases by a factor of 5.0 while the shear stress increases by a factor of 2.3. This effect of pressure is interpreted as follows: As pressure is increased the amount of slip taking place on a given plane is decreased thus causing more slip planes to operate and increasing the likelihood that each molecule will be in a disordered region. Greater distortions of the lattice are also a result of increased pressure but this factor already has been accounted for in terms of the increase in the shear stress.

The data obtained with shear at 10,000 atm. are not of sufficient accuracy to make an unambiguous determination of the order of the reaction. As expected, the data for the thermal reaction are best fitted by first-order kinetics.

The fact that the oxalate complex does not react under shear is attributed to a shift in equilibrium with pressure. At a pressure of 50 atm. of carbon dioxide ferrous oxalate in potassium oxalate solution is partially converted to potassium tris-(oxalato)-ferrate(III).[12] The necessity of estimating several physical properties made impossible a reliable estimate of the sign of the volume change involved in the reaction expressed by eq. 3.

We are obliged to J. C. Bailar, Jr., for lending us some of the samples and for useful discussions.

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[11] P. I. Byal'kevich, *Vestnik Akad. Nauk, Beloruss S.S.R.*, **1**, 71 (1953); also *C. A.*, **49**, 5089i (1955).

[12] C. Schaper, *Z. physik. Chem.*, **72**, 308 (1910).

NOTES

ENERGY INTERACTIONS IN THE FLUOROCHLOROMETHANES[1]

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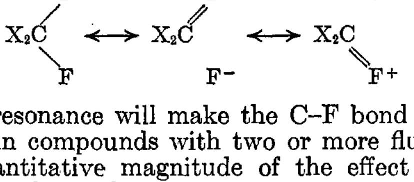
It is a common approximation to assume constant properties for a bond between a given pair of kinds of atoms regardless of their surroundings. Many examples of constant bond distances could be cited. If bond energies are constant for the C–X and C–Y bonds, then the redistribution reaction for the various compounds CX_nY_{4-n} is governed in good approximation by purely random statistics. Calingaert[2] has found several examples of this type, and Forbes and Anderson[3] showed that the chlorobromomethane system was random. Of course, this can only be an approximation—even isotope redistribution reactions are known to deviate minutely from randomness.

In contrast, however, the reported values of the C–F bond length vary rather systematically over an appreciable range. Table I shows several examples. Where there is but a single fluorine, the C–F distance is about 1.42 Å., but with three or four fluorines present the distance is near 1.32 Å. Brockway[4] explained this effect by the double bond–no bond resonance.



This resonance will make the C–F bond energy greater in compounds with two or more fluorines. The quantitative magnitude of the effect is not readily predicted, however.

In the lighter paraffin hydrocarbons there are significant deviations from constant bond energies but these have been explained by non-bonded interactions arising from electron correlation.[5] These were treated by the same methods that were developed for intermolecular forces. It is interesting to apply this method to the fluorochloromethanes and

[1] This research was assisted by the American Petroleum Institute through Research Project 50.

[2] G. Calingaert, *et al.*, *J. Am. Chem. Soc.*, **61**, 2748, 2755, 2758, 3300 1939); **62**, 1099, 1104 (1940).

[3] G. S. Forbes and H. H. Anderson, *ibid.*, **66**, 931 (1944).

[4] L. O. Brockway, This Journal, **41**, 185 (1937).

[5] K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4565, 4844 (1956).

TABLE I

BOND DISTANCES, Å.

Compound	C–F distance	C–Cl distance	Ref.
CF_4	1.323	...	*a*
CF_3Cl	1.323	1.765	*b*
CHF_3	1.332	...	*c*
CF_2Cl_2	1.35 ± 0.03	1.74 ± 0.03	*d*
CHF_2Cl	1.36 ± .03	1.73 ± .03	*d*
$CFCl_3$	1.44 + .04	1.76 ± .02	*e*
	1.40 ± .04	1.76 ± .02	*d*
$CHFCl_2$	1.41 ± .03	1.73 ± .04	*d*
CCl_4	...	1.77 ± .01	*f*

[a] L. O. Brockway, *Acta Cryst.*, **7**, 682 (1954). [b] D. K. Coles and R. H. Hughes, *Phys. Rev.*, **76**, 858 (1949). [c] S. N. Ghosh, R. Trambarulo and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). [d] L. O. Brockway, This JOURNAL, **41**, 185 (1937). [e] J. Wouters and M. de Hemptinne, *Nature*, **141**, 412 (1938). [f] I. L. Karle and J. Karle, *J. Chem. Phys.*, **17**, 1052 (1949).

the chlorobromomethanes. The calculation included all halogen–halogen interactions and used the formula found most successful previously.

$$\Delta E_{AB} = -\frac{3e\hbar}{2m^{1/2}R^6}\cdot\frac{\alpha_A\alpha_B}{[(\alpha_A/N_A)^{1/2} + (\alpha_B/N_B)^{1/2}]}$$

Here the polarizability α was given the values listed by Ketelaar,[6] 0.38, 2.28 and 3.34, all $\times 10^{-24}$ cm.^{3}, for F, Cl and Br, respectively. In the earlier work the effective number of polarizable electrons N was found to be 8 for neon and 11 for argon and krypton. Accordingly we chose the values 7 for fluorine and 10 for chlorine and bromine. The following pairwise interaction energies are obtained

$$\begin{aligned}\Delta E_{F-F} &= -1.0 \text{ kcal./mole}\\ \Delta E_{F-Cl} &= -1.6\\ \Delta E_{Cl-Cl} &= -3.5\\ \Delta E_{Cl-Br} &= -3.5\\ \Delta E_{Br-Br} &= -3.6\end{aligned}$$

It is apparent from these values that the Cl–Br interaction is very close to the mean of the Cl–Cl and Br–Br values. Consequently, no significant deviation from a random distribution will arise from this cause. However, the F–Cl interaction is less than the mean of the F–F and Cl–Cl values by 0.65 kcal./mole. This is a substantial energy difference at or near room temperature. The effect on the distribution equilibrium is to make the intermediate compounds unstable as compared to CCl_4 and CF_4. This will reinforce the resonance effect mentioned above, and leads to the prediction of a significantly non-random distribution equilibrium for the fluorochloromethanes.

We hoped to obtain a quantitative measurement of the equilibrium distribution, but side reactions never were eliminated. Consequently our results constitute only a qualitative confirmation of our expectation, and we will present them very briefly. Details may be found elsewhere.[7]

Henne and others[8] have shown that anhydrous aluminum chloride accelerates the disproportionation of fluorochloromethanes. Unfortunately, this is not a pure catalysis—some fluorine is usually exchanged for the chlorine of the aluminum chloride. We found that after repeated exposure of the aluminum halide to CF_2Cl_2, for example, the amount of side reaction dropped to a low value but the desired reactions were then relatively slow.

The analysis was by gas chromatography. Reaction times were 20–100 hr. at 127°. Runs starting with pure CF_2Cl_2 yielded mostly CF_3Cl and CCl_4 with only about 2% of CF_2Cl_2 and 1% of $CFCl_3$. Production of CF_4 was very slow but gave no indication of an approach to equilibrium. Also there was substantially more Cl and less F in the products than the reactants. In later runs starting with CF_3Cl and CCl_4 this exchange with the aluminum halide was small, but the approach to equilibrium was too slow to yield precise and reliable results. Nevertheless, the apparent equilibrium constants were reasonably concordant with those calculated from the runs starting with CF_2Cl_2. The values are

$$K_1 = \frac{(CF_2Cl_2)^3}{(CF_3Cl)^2(CCl_4)} \qquad \log K_1 = -3.0$$

$$K_2 = \frac{(CFCl_3)^3}{(CF_3Cl)(CCl_4)^2} \qquad \log K_2 = -4.5$$

Because of the side reaction with the aluminum halide, no limit of error can be placed upon these values, but it seems unlikely that either log K is in error by more than one unit. A random distribution yields log $K_1 = +1.13$ and log $K_2 = +1.20$. Thus our results differ from the random distribution by 4 powers of ten for K_1 and by nearly 6 powers of ten for K_2.

If we take the non-bonded electron correlation energies given above together with these rough equilibrium values, we obtain the following differences in C–F bond energies. The C–Cl bond energy is assumed to be constant.[9]

$$\begin{aligned}E_{C-F}(CF_3Cl) - E_{C-F}(CF_2Cl_2) &= \left(\frac{2.3RT}{6}\right)(4.1) - 0.65\\ &= 0.6 \text{ kcal./mole}\\ E_{C-F}(CF_3Cl) - E_{C-F}(CFCl_3) &= \left(\frac{2.3RT}{3}\right)(5.7) - 1.30\\ &= 2.2 \text{ kcal./mole}\end{aligned}$$

There are six C–F bonds involved in reaction of K_1 and three for K_2. T is 400°K. Six F–Cl interactions are introduced in each reaction. Thus the C–F bond energy increases by about 1.6 kcal./mole from $CFCl_3$ to CF_2Cl_2 and by another 0.6 kcal./mole in CF_3Cl. These values are to be attributed to the double bond–no bond resonance.

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(6) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Pub. Co., Amsterdam and Houston, 1953, p. 90.

(7) D. E. Petersen, Ph.D. Dissertation, University of California, 1957.

(8) A. L. Henne, *et al.*, *J. Am. Chem. Soc.*, **60**, 864, 1697 (1938); see also U. S. Patents 2,426,637, 2,426,638 and 2,637,748.

(9) The Referee very kindly mentioned unpublished values of bond distances which are more accurate than those in Table I. The only change in the qualitative picture is the appearance of a slight trend in C–Cl distance. Since the change in C–Cl distance is still small compared to that in C–F distance, the assumption of constant C–Cl bond energy appears to be a good first approximation.

THE MELTING POINT OF CADMIUM SULFIDE

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In a previous note[1] a redetermination of the

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(1) A. Addamiano and P. A. Dell, THIS JOURNAL, **61**, 1020 (1957).