adducts. Sensitized irradiation gives the previously known[6] 2-propanol adduct.

Cycloaddition could be sensitized by triphenylene ($E_T \sim 67$ kcal/mole) and acenaphthene ($E_T \sim 59$ kcal/mole, $\Phi = 0.2$), both of which have lower triplets than benzophenone. This was, in the case of acenaphthene, shown to be because of singlet–singlet energy transfer. In an EPA[7] glass at 77°K 0.1 *M* cyclopentenone quenched acenaphthene fluorescence by about 90% and increased the acenaphthene phosphorescence about threefold. Excluding the possibility of cyclopentenone facilitating intersystem crossing in the hydrocarbon, it would appear that singlet energy is being transferred from the hydrocarbon to cyclopentenone which then undergoes intersystem crossing, followed by partial transfer of triplet energy to the hydrocarbon.[8]

That the singlet (S_1) is not, nonetheless, the active cycloaddition species is shown by the fact that cycloaddition can be sensitized by high-energy sensitizers (see Figure 1) which, because of their low singlet energies or high rate of intersystem crossing, or both, are unlikely to transfer singlet excitation. From these results it will be seen that a triplet energy of about 73 kcal/mole or more is necessary to generate this species, but that at this level energy transfer is not yet diffusion controlled. Since the excited cyclopentenone produced is not in its additively inactive T_1 state ($E_T \sim 61$ kcal[9]) it would seem to be required that the excited reactive species produced is cyclopentenone in its T_2 state.[10] Hence cycloaddition—or collapse to yet another active species—is a process which can compete with internal conversion to T_1.[11]

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[7] EPA is ethyl ether–isopentane–ethyl alcohol in volume ratio of 5:5:2. Available from American Instrument Co., Silver Spring, Md.

[8] For a comparable example see P. A. Leermakers, G. W. Byers, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 2670 (1963).

[9] The phosphorescence of triphenylene (67 kcal/mole) is quenched by cyclopentenone, and emission studies in the presence of naphthalene suggested that T_1 for cyclopentenone was near that of naphthalene (61 kcal/mole). Professor P. A. Leermakers informs us that he has determined the triplet energy of cyclopentenone and found it to be near 61 kcal/mole. We thank Professor Leermakers cordially for this information.

[10] In a constrained cyclopentenone Professor W. Herz has observed n,π^* emission with a 0–0 band at 74.5 kcal/mole. We thank Professor Herz for telling us in advance of publication.

[11] For a pertinent analogy in the photochemistry of 9-anthraldehyde see N. C. Yang, *Pure App. Chem.*, **9**, 591 (1964).

[12] On leave from C. N. R. S. (France).

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Received August 28, 1967

Catalysis and Inhibition of the Hydrolysis of Xenon Difluoride

Sir:

The hydrolysis of xenon difluoride in alkaline, neutral, and acidic solutions leads to a simultaneous redox reaction; that is, the hydrolysis means, in fact, the oxidation of water. Recently, Appelman and Malm[1] studied the effect of different salts and acids on the rate of hydrolysis. Unfortunately, the comparison of most of their experimental results is impossible because more than one parameter was varied simultaneously and the observed effect was evidently the resultant of different factors. Our experiments were aimed at learning the effect of pH, of ionic strength, and of different cations and anions.

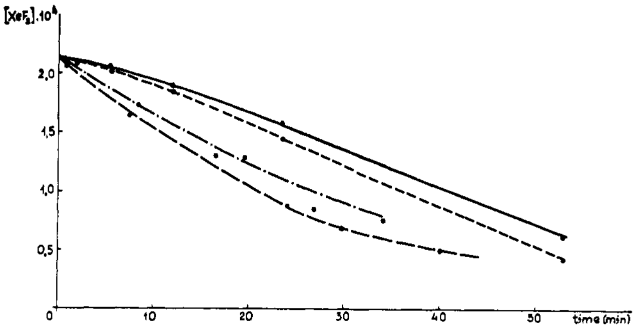

Figure 1. Effect of metal ions on the decomposition of xenon difluoride at pH 3.1: ———, no metal ion added; - - - - -, La^{3+}; – · – ·, Be^{2+}; – – – –, Th^{4+}.

The mass spectrometrically determined purity of XeF_2 was 99.9%.[2] Stock solutions of 10^{-2} *M* were made just before each experiment; the initial concentration of XeF_2 in the reaction mixture was $\sim 2 \times 10^{-4}$ *M* in each case. The concentration of nondecomposed XeF_2 was determined time to time by adding acidified KI to the aliquots of the reaction mixture and then measuring the absorbancy of the solution at 350 nm. Twice distilled water and reagents of CP quality were always used. Since the exploratory experiments proved that the accelerating effect of surface of the glass vessels is negligible,[3] all experiments, except with fluoride in acidic solution, were performed using glass vessels. In the latter case a polyethylene flask was used as the reaction vessel. The temperature was always 22 ± 1°.

The rate of the hydrolysis as a function of pH shows a minimum in the pH range 4–9. The determination of the exact position of the rate minimum is difficult, there being no great difference in the rate in this range, and the application of buffer solutions may result in some other effects (see below).

The effect of some cations forming stable complexes with fluoride was studied. Figure 1 shows the effect of La^{3+} (8×10^{-3} *M*), Be^{2+} (8×10^{-4} *M*), and Th^{4+} (8×10^{-4} *M*) at pH 3.1.

The accelerating effect of Al^{3+} was observed at pH 2.1. The order of the accelerating effect of these metal ions is the same as the order of the stability constants[4] of their monofluoro complexes: $Th^{4+} > Al^{3+} > Be^{2+} > La^{3+}$. The phenomenon is analogous to the catalysis of aquation reaction of complexes. The basic reason of the accelerating effect is evident; however, it is not clear whether a fluoro-bridged intermediate (F–Xe–Fe–Me^{n+}) itself or the species XeF^+ reacts with water.

We observed that fluoride ions considerably catalyzes the hydrolytic decomposition. The effect is more pronounced in slightly alkaline than in weakly acidic solution (Figure 2). The catalytic effect of carbonate and

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[1] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297; (1964).

[2] Xenon difluoride was prepared by the Central Research Institute of Physics, Budapest, Hungary. The gift is gratefully acknowledged.

[3] The effect of large surfaces of glass and silica is considerable.

[4] L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

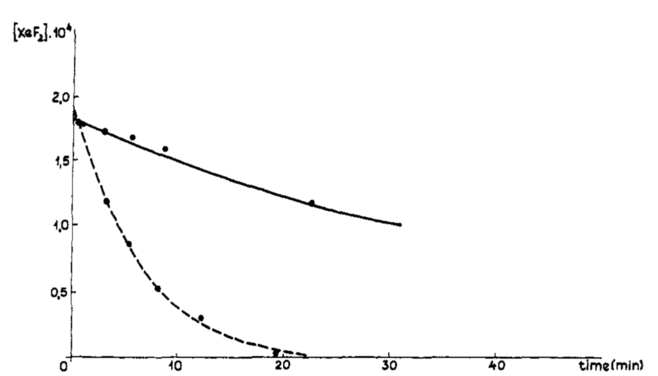

Figure 2. Effect of potassium nitrate and potassium fluoride on the decomposition of xenon difluoride: ———, 1 M KNO_3, 0.06 M $KHCO_3$, pH 8.4; - - - -, 1 M KF, 0.06 M $KHCO_3$, pH 8.4.

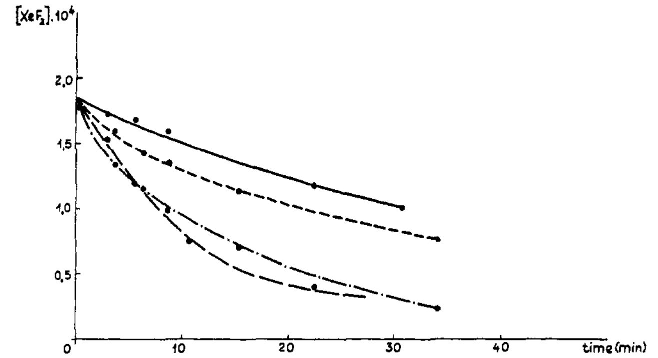

Figure 3. Effect of ionic strength on the decomposition of xenon difluoride at pH 8.4: ———, 1 M KNO_3, 0.06 M $KHCO_3$; - - - -, 0.2 M KNO_3, 0.06 M $KHCO_3$; - - - - -, 2 M $NaClO_4$, 0.06 M $NaHCO_3$; - · - ·, 0.2 M $NaClO_4$, 0.06 M $NaHCO_3$.

hydrogen carbonate as well as phosphate and hydrogen phosphate ions is even much greater.[5] Besides these specific ionic effects it was observed that when the ionic strength is increased the reaction is retarded (Figure 3).

The accelerating effect of the different anions can be formally interpreted by the formation of reactive complex ions; however, more detailed investigation is necessary to give a satisfactory explanation. These and analogous experiments with other xenon fluorides are in progress in collaboration with the Central Research Institute of Physics of the Hungarian Academy of Sciences.

(5) The catalytic effect of these ions was also observed by Dr. E. H. Appelman (personal communication, Aug 11, 1967).

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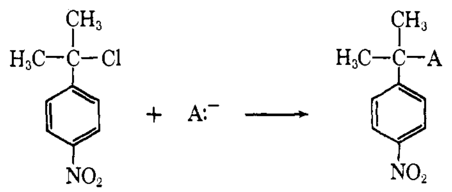
Received June 13, 1967

New and Facile Substitution Reactions at Tertiary Carbon. The Displacement of a Nitro Group from a Saturated Carbon Atom

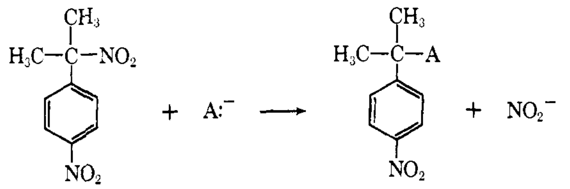
Sir:



(1)

I

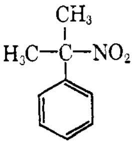
We have recently reported a new type of substitution process at tertiary carbon in which the chlorine of p-nitrocumyl chloride (I) is replaced by a variety of anions (eq 1).[1] We now wish to describe an even more striking set of reactions in which the aliphatic nitro group of α,p-dinitrocumene (II) is displaced (eq 2). The reaction of eq 2 is noteworthy not only because it involves substitution at a tertiary carbon atom but also because it is a reaction without precedent—the displacement of a nitro group from a saturated carbon atom.



(2)

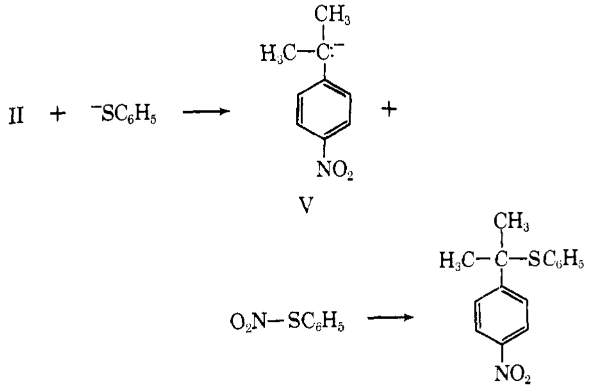
II III

For example, the reaction of II with sodium thiophenoxide in DMF (or in DMSO) solution at 25° is complete in 20 min and produces the pure tertiary sulfide III ($A = SC_6H_5$) in 96% yield. In contrast, α-nitrocumene (IV) is not attacked by sodium thiophenoxide under these conditions.



IV

Since substitution at the tertiary carbon is facilitated by a p-nitro group, the possibility that the thiophenoxide ion displaces on the aliphatic nitro group to give carbanion V, and that this in turn gives the tertiary sulfide (eq 3), must be considered. If carbanion V is indeed an intermediate, it would be anticipated that, on conducting the reaction in DMSO containing 20 moles of methanol for each mole of II, a significant fraction of the carbanions would be scavenged by the methanol.[2] This is not what is observed; in methanolic DMSO a



(3)

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[1] N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Am. Chem. Soc.*, **89**, 725 (1967).

[2] I. J. Borowitz and R. Virkhaus, *ibid.*, **85**, 2183 (1963).