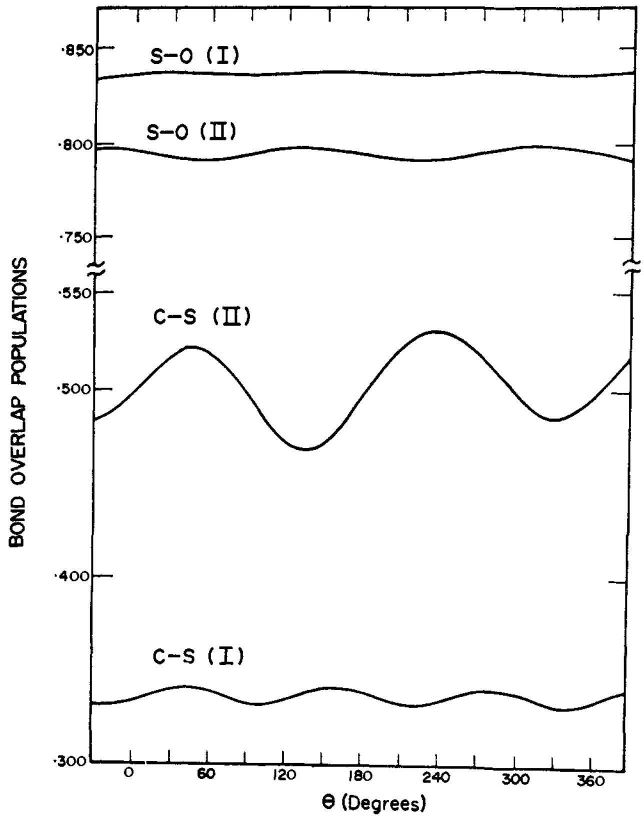

Figure 4. Bond overlap populations as a function of rotational angle (θ) about the C–S bond for I and II.

configuration will depend upon its specific environment in the molecule. We hope that experiments in progress will provide information on this point.[12]

Acknowledgments. We thank the Institute of Computer Science of the University of Toronto for making their facilities available to us and the National Research Council of Canada for financial support. Special thanks go from S. W. and A. R. to Professor D. J. Leroy for his kind hospitality.

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(12) The data of Cram and Pine[13] are consistent with this prediction. These workers found (*R*)-2-octyl phenyl (*S*)-sulfoxide[14] to undergo H–D exchange in DMSO by an inversion mechanism ($k_e/k_\alpha = 0.58$); the epimeric (*R*)-2-octyl phenyl (*R*)-sulfoxide[14] exchanged by a retention mechanism ($k_e/k_\alpha = 1.4$).

(13) D. J. Cram and S. H. Pine, *J. Am. Chem. Soc.*, **85**, 1096 (1963).

(14) The configurational assignments in Cram and Pine's paper have been reversed by the work of K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simons, and A. L. Ternay, *J. Am. Chem. Soc.*, **87**, 1958 (1965).

(15) Holder of a National Research Council Studentship 1966–1967.

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Cyclopentenone Photocycloaddition. A Reaction from a Higher Triplet State[1]

Sir:

There has been considerable interest expressed in the recent literature on the nature and multiplicity of the reacting species in the photocycloadditions of excited α,β-unsaturated ketones[2] and in particular those of cyclopentenone.[2a,b,3] It has been concluded in the latter case[2a,b] that a triplet is involved in dimerization. We report here evidence that in the addition of cyclopentenone to cyclohexene (which gives cyclobutane adducts of the type reported[3] for the addition to cyclopentene) the agent concerned is cyclopentenone in its T_2 state (or a species derived from it) and that the lowest triplet, T_1, is ineffective in cycloaddition.

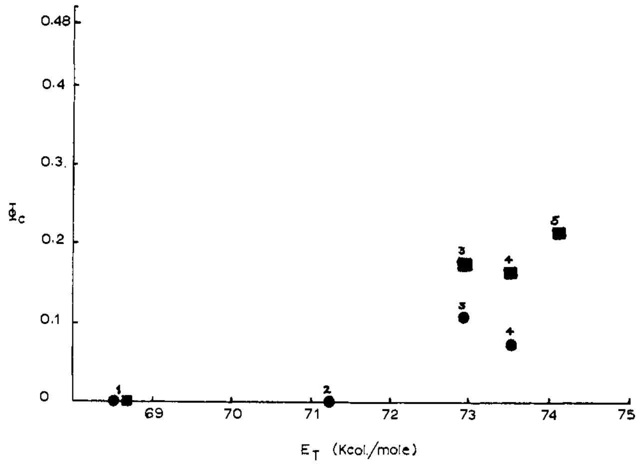

Figure 1. Quantum yields of cycloaddition (Φ_c) with sensitizers irradiated at 313 mμ. Concentration of sensitiser *ca.* 1 *M;* concentration of cyclopentenone 0.1 *M* (●), 0.3 *M* (■). Sensitizers: (1) benzophenone, (2) 4-bromoacetophenone, (3) 4-methylacetophenone, (4) acetophenone, (5) cyclopropyl phenyl ketone (uncorrected for triplet yield or transfer to cyclohexene).

The photocycloaddition of cyclopentenone to cyclohexene (solvent) proceeds in high quantum yield ($\Phi = 0.48$).[4] Using benzophenone as a sensitizer ($E_T \sim 69$ kcal/mole) no cycloaddition was observed ($\Phi < 0.01$), but triplet energy was nonetheless transferred to the cyclopentenone. This was shown (a) by the fact that (0.11 *M*) benzophenone phosphorescence is quenched (in ether–ethanol 3:1, matrix at 77°K) by 2 *M* cyclopentenone, and (b) because the photoreduction of benzophenone by 2-propanol, a well-studied triplet process,[5] is quenched by the addition of cyclopentenone.[6] A linear Stern–Volmer plot (over a range of 0.005–0.1 *M* cyclopentenone) was obtained whose slope (55 M^{-1}) indicated close to diffusion-controlled quenching. On the assumption that benzophenone excites cyclopentenone to its lowest triplet this species apparently does not cycloadd. Direct irradiation of cyclopentenone in 2-propanol–cyclohexene gives cyclo-

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(1) Photochemical Synthesis. XX.

(2) (a) P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966); (b) H. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *ibid.*, **86**, 5570 (1964); (d) O. L. Chapman, "Organic Photochemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1967, p 304 *et seq.*; (e) E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 3482 (1967).

(3) P. E. Eaton, *ibid.*, **84**, 2454 (1962).

(4) Irradiation at 313 mμ. The effect of the substrate and the solvent in cyclopentenone addition has been studied in some detail and a report will be submitted for publication.

(5) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961); A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2039, 2051 (1963); J. N. Pitts, H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(6) M. Pfau, R. Dulou, and M. Vilkas, *Compt. Rend.*, 1817 (1962).

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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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.

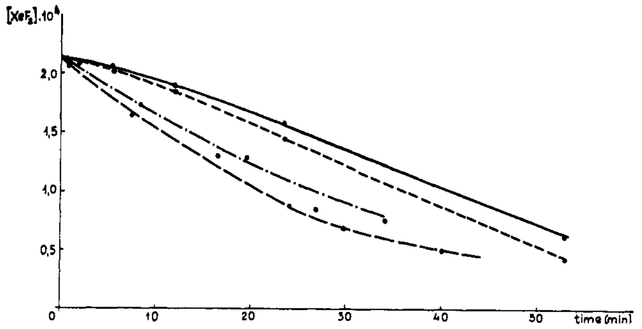

Figure 1. Effect of metal ions on the decomposition of xenon difluoride at pH 3.1: ———, no metal ion added; - - - - -, La^{3+}; – · – ·, Be^{2+}; – – – –, Th^{4+}.

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.