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Short Communication

Photophysics of halogenated ketones: Radiative and and non-radiative decay

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The photophysical and photochemical processes consequent upon excitation of simply substituted acetones to their first excited singlet states have been the subject of several recent investigations[1–5]. Excitation to the zeroth or low-lying vibrational levels of the singlet state produces a non-dissociative level, from which the energy dissipation processes are fluorescence and intersystem crossing to the triplet manifold[3,4]. By a study of the fluorescence quantum yields and fluorescence decay times of a variety of halogenated acetones in the gas phase the effect of halogen substitution upon the absolute rate constants for radiative and non-radiative decay of the singlet states may be determined, and such results are reported here.

Fluorescence decay times were measured using a time-correlated photon-counting system described earlier[6]. Fluorescence quantum yields were measured relative to that for hexafluoroacetone vapour[2]. The compounds were purified by preparative gas chromatography or distillation *in vacuo*.

Values of quantum yields of fluorescence, decay times and rate constants k_r and k_{nr} derived from these data in the usual way are shown in Table 1. Also shown in Table 1 are the values of k_r expected on the basis of the Strickler–Berg formula, $k_r(SB)$[5,7]. A comparison of these results with the experimental values is interesting. The Strickler–Berg equation[7] is applicable strictly only to allowed transitions, and thus the agreement between $k_r(SB)$ and the experimental value of k_r may be used as an indication of the nature of the radiative transition. In the present case, the transition is nominally of n–π^* character which for formaldehyde is orbitally forbidden and made allowed by the out-of-plane deformation which distorts the planar ground state into the pyramidal geometry of the $n\pi^*$ excited state. Halpern and Ware[5] have shown that values of k_r and $k_r(SB)$ for acetone,

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TABLE 1

RATE CONSTANT DATA FOR EQUILIBRATED $^1n\pi^*$ STATES OF HALOGENATED KETONES

Compound	Pressure (Torr)	Wavelength of excitation (nm)	Φ_f	τ_f (ns)	k_r (SB) $\times 10^{-5}$ (s^{-1})	k_r $\times 10^{-5}$ (s^{-1})	k^a_r $\times 10^{-7}$ (s^{-1})	Ref.
Acetone	—	—	0.0012	2.4	1.0	5	42	5
Acetone-d_3	—	—	0.0016	3.4	0.86	4.7	29	5
Fluoroacetone	50	310	0.0011	~ 2*	0.7	~ 4.5	~ 50	5
1,1,1-Trifluoroacetone	200	310	0.0010	4.0	0.6	2.5	25.0	This work
Hexafluoroacetone	—	357.7	0.0185	84	0.56	2.2	1.2	5
Choropentafluoroacetone	40	340	0.021	36.1	3.8	5.6	2.7	This work
1,3-Dichlorotetrafluoro-acetone	80	340	0.015**	30.0	6.0	5.0	3.3	This work
1,1,3-Trichlorotri-fluoroacetone	40	340	0.004	12.5	3.8	3.4	8.0	This work

*Decay time too short to be measured reliably.

**In a previous publication this value was wrongly given as 0.07 [P. A. Hackett and D. Phillips, *J.C.S. Faraday Trans. I*, 68 (1972) 323].

acetone-d_6 and hexafluoroacetone are consistent with this model in that the rate constant values are not in agreement (see Table 1) and moreover, the experimental values of k_r are approximately proportional to the promoting mode frequency in the lower state as would be expected from Albrecht's theory of vibronic transitions[8]. The expected effect of substitution of a heavier atom in the molecule is therefore to reduce the value of k_r by reducing the frequency of the promoting mode. Table 1 shows that the results for fluoroacetone and 1,1,1-trifluoroacetone are consistent with this expectation. Replacement of one or more fluorine atoms in the hexafluoroacetone structure by chlorine atoms would on the basis of the arguments above be expected to cause further reduction of k_r for these compounds compared with that for hexafluoroacetone. However, the opposite trend is noted from the data in Table 1. A possible explanation for this effect is that there is an interaction of the n electrons on the α-chlorine atoms, or alternatively of the carbon-chlorine σ^* orbitals, with the π system of the carbonyl group. This would result in increased oscillator strength in the nominal n–π^* transition leading to increase in extinction coefficients and k_r. Some support is lent to this hypothesis in that for the three chlorinated acetones studied here, values of k_r(SB) and k_r are in much closer agreement than the fluorinated compounds, implying that the electronic transition is of an allowed character.

The mixing of chlorine non-bonding electrons, or carbon–chlorine σ^* molecular orbitals into the $n\pi^*$ transition could have important consequences on the rate of non-radiative processes. In the case of equilibrated chloropentafluoroacetone and 1,3,-dichlorotetrafluoroacetone this non-radiative process can be unambiguously defined as intersystem crossing since the triplet state yield under these conditions was shown to be close to unity[3,4]. It is not unreasonable to suppose that this is also the major fate of the 1,1,3,-trichlorotrifluoroacetone molecules.

Halpern and Ware[5] found k_{nr} to vary from 41.7×10^7 s^{-1} in acetone, to 29.4×10^7 s^{-1} in acetone-d_6 and 1.2×10^7 s^{-1} in hexafluoroacetone. They attributed this trend to an "isotope effect". It is interesting to note that the non-radiative rate constant for trifluoroacetone fits into the series. The intersystem crossing rate constant for this compound is 25×10^7 s^{-1}. However, as with the radiative rates the non-radiative rate constants in the series of chlorofluoro ketones show an opposite trend compared with that predicted on the basis of Halpern and Ware's analysis. Factors influencing the rate of non-radiative decay to the triplet state include magnitude of vibronic coupling, spin-orbit coupling, Franck–Condon factors, and density of states. It is not possible at this stage to attribute the observed trend in k_{nr} upon progressive chlorination specifically to any of these factors. However, El-Sayed has shown[9] that heavy atoms should have a negligible effect on n–π^* transitions of carbonyls, assuming that the orbitals involved in the $n\pi^*$ transition have zero coefficients on the halogen atoms. Clearly if the configurational interaction tentatively proposed to explain the variation in radiative rate

constant is significant the spin orbit coupling matrix elements will contain one centre terms on the halogens, and "heavy atom" effects might be manifested.

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1 J. R. Majer, C. Olaveson and J. C. Robb, *J. Chem. Soc.(A)*, (1969) 893; *ibid.*, (B) (1971) 48; R. Bowles, J. R. Majer and J. C. Robb, *Trans. Faraday Soc.*, 58 (1962) 1541, 2394; J. R. Majer and J. P. Simons, *Adv. Photochem.*, 2 (1964) 137.
2 D. A. Whytock and K. O. Kutschke, *Proc. Roy. Soc.*, A306 (1968) 503; A. Gandini and K. O. Kutschke, *ibid.* A306 (1968) 511; A. Gandini, D. A. Whytock and K. O. Kutschke, *ibid.*, A306 (1968) 529, 541.
3 H. S. Samant and A. J. Yarwood, *Can. J. Chem.*, 48 (1970) 2611, 2937.
4 P. A. Hackett and D. Phillips, *J.C.S. Faraday Trans. I*, (1972) 68, 323, 329, 335.
5 A. M. Halpern and W. R. Ware, *J. Chem. Phys.*, 53 (1970) 1969; *ibid.*, 54 (1971) 1271.
6 G. M. Breuer, P. A. Hackett, D. Phillips and M. G. Rockley, *J.C.S. Faraday Trans. II*, 68 (1972) 1995.
7 S. Strickler and R. A. Berg, *J. Chem. Phys.*, 37 (1962) 814.
8 A. Albrecht, *J. Chem. Phys.*, 33 (1960) 156.
9 M. F. A. El-Sayed, *J. Chem. Phys.*, 41 (1964) 2462.