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Photochemical reactions of monomeric and dimeric radical cations of acetone in freon matrices at 77 K

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Monomeric [$\lambda_{max} \simeq 435$ nm, $\varepsilon_{max} \simeq (3.6 \pm 0.6) \times 10^3$ dm^3 mol^{-1} cm^{-1}] and dimeric [$\lambda_{max} \simeq 715$ nm, $\varepsilon_{max} \simeq (9.4 \pm 1.2) \times 10^3$ dm^3 mol^{-1} cm^{-1}] radical cations of acetone in a freon matrix at 77 K under the action of light react to form matrix radical cations and acetonyl radicals CH_2COMe with quantum yields of $\Phi > (4.0 \pm 1.0) \times 10^{-3}$ and $\Phi > (2.0 \pm 1.0) \times 10^{-2}$, respectively.

Radical cations (RC) are one of the most important intermediates of many radiation, photochemical, oxidizing and catalytic processes. At the same time there is little reported data concerning the reactivity of electronically excited RC.[1] Information about the absorption spectra of RC of different organic compounds and the quantum yields of their photochemical reactions is practically absent in literature.

The absorption band at $\lambda \simeq 715$ nm in irradiated solutions of acetone in *n*-butylchloride had been previously assigned to acetone RC.[2] The different behaviour of dimeric and monomeric RC of acetone in frozen freon solutions under the action of light has been noted.[3]

The purpose of the present investigation was to obtain data about the efficiency and mechanism of the photochemical reactions of acetone RC with different structures stabilized in a glassy freon matrix at 77 K.

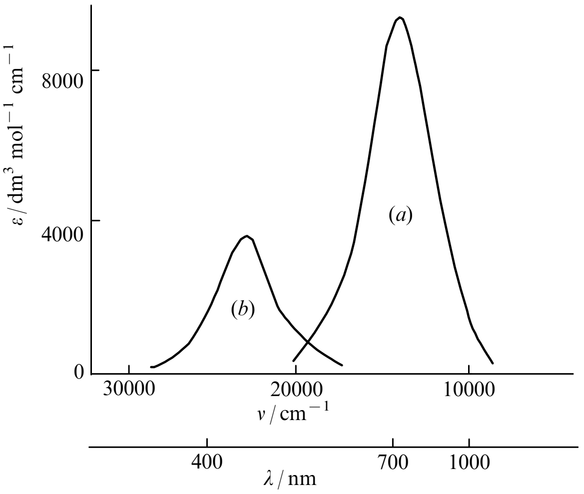

Figure 1 Absorption spectra of dimeric (*a*) and monomeric (*b*) acetone RC in irradiated solutions of acetone (1%) in the FM at 77 K.

Having been deaerated to 10^{-4} Torr, acetone solutions (0.1–10 vol.%) in a glassy freon mixture [1 : 1 vol., $CFCl_3$ (freon-11) and CF_2BrCF_2Br (freon-114B2)] (FM) at 77 K were irradiated with X-rays (E = 50 kV); the total absorbed dose was 0.5–2 kGr. The EPR and optical spectra of the intermediates formed were recorded with the use of E3 Varian radiospectrometer and Specord M-40 and Shimadzu 3100 spectrophotometers on the same samples, with an optical pathway of 0.3 cm. A high pressure mercury lamp equipped with a narrow-band glass filter (λ = 436 nm, $\Delta\nu_{1/2} \simeq 3000$ cm^{-1}) and interference filter (λ = 752 nm, $\Delta\nu_{1/2} \simeq 500$ cm^{-1}) was used as the source of light. The absolute intensity of light was determined by ferric oxalate actinometry (λ = 436 nm) and the system triphenylamine–tetranitromethane (λ = 752 nm).[4] The values of light intensity were 1.6×10^{-4} einstein cm^{-3} s^{-1} (λ = 436 nm) and 1.35×10^{-5} einstein cm^{-3} s^{-1} (λ = 752 nm). The volume of each sample in our experiments was 0.13 cm^{-3}. The values of the extinction coefficients and the quantum yields were calculated from 6–12 experimental results; the error value was obtained with a confidence limit of 0.95.

The exposure of acetone solutions (0.1–10%) in the FM to irradiation at 77 K results in the appearance of an absorption band with $\lambda_{max} \simeq 715$ nm which can be assigned to dimeric acetone radical cations by analogy with reported data[2] (Figure 1*a*).

The correlation observed in concentrated (1–10%) solutions between the change of the absorption band intensity ($\lambda_{max} \simeq 715$ nm) with the change in concentration of the paramagnetic centres possessing a singlet signal [which have a weak g-factor anisotropy (g_{av} = 2.0032) in the EPR spectra and are assigned[3] to dimeric acetone RC] made it possible to determine both the extinction coefficient and oscillator strength in this electron transition (Table 1). The concentration of dimeric acetone RC in our experiments was (2.5–8.0) $\times 10^{-4}$ mol dm^{-3}. The action of light with λ = 752 nm on the dimeric acetone RC results in their decay and the formation of CH_2COMe radicals [a(2H) = 20.5 G] accompanied by a constant total concentration of paramagnetic centres. The dependence of the kinetics of dimeric acetone RC decay on the absorbed dose has a distinct bimodal character, being indicative of the kinetic non-equivalence of reacting particles in the solid phase (Table 2). The mechanism of formation of CH_2COMe radicals during the photolysis of RC was found to be connected with hydrogen atom transfer in the dimer and to be identical to that observed in their thermal transformation.[3]

$$(Me_2CO^{+\cdot})_2 \longrightarrow CH_2COMe + Me_2COH^{+} \qquad (1)$$

Hydrogen atom transfer to monomeric acetone RC from isopropanol molecules [reaction (2)] was determined with the use of a spin trapping method reported earlier.[5]

$$Me_2CO^{+\cdot} + Me_2CHOH \longrightarrow Me_2COH^{+} + Me_2COH \qquad (2)$$

The possibility of a proton transfer reaction in the photoconversion of dimeric acetone RC can be excluded from consideration because, for the RC, it occurs from the position with maximum spin density,[6] whereas observed extremely small values of coupling constants for methyl groups in the EPR spectrum of dimeric acetone RC (< 2 G)[7] indicate a low spin density in these positions. In this case the nature of the observed kinetic non-equivalence can be connected either with a different structure of dimeric RC or with the possibility of photochemically inactive photons energy restorating the distribution function of reacting RC.[8]

After photobleaching of the dimeric acetone, RC irradiated acetone solutions (0.1–10%) in the FM at 77 K exhibit an absorption band with a maximum at about $\lambda \simeq 435$ nm (Figure 1*b*). The change in intensity of this band for solutions with a concentration of acetone in the range 0.1–1% correlates with the concentration change of paramagnetic centres possessing a singlet signal with g-factor anisotropy which can be assigned to the monomeric acetone RC according to reported data.[9] The concentration of monomeric acetone RC in our experiments was (2.0–4.0)$\times 10^{-4}$ mol dm^{-3}. Monomeric acetone RC were shown to disappear under the action of light with λ = 436 nm. The kinetics of their decay have a distinct bimodal character, as in the case of dimeric RC (Table 2). It is important to note that the decrease in absorption intensity of monomeric acetone RC is accompanied by an increase in absorption in the region $\lambda \simeq 370$ nm, which can be assigned to RC of freon-114B2.[10] Thus the action of light on monomeric acetone RC leads to charge-transfer to the matrix molecule. The estimated value of the extinction coefficient of freon-114B2 RC is about 7×10 dm^3 mol^{-1} cm^{-1}. This is in good agreement with the value of $\simeq 10^4$ dm^3 mol^{-1} cm^{-1} determined independently for the irradiated FM. The formation of freon RC is energetically possible because the photon energy, $E_{h\nu}$ = 2.8 eV, is higher than the difference between the values of the ionization potentials for acetone (9.69 eV) and that of the freons used (11.4 for freon-114B2 and 11.77 eV for freon-11). Photochemical reactions of monomeric RC in diluted (0.1–1%) acetone solutions are not accompained by the formation of radicals (these processes lead to a decrease of the total concentration of paramagnetic centres), whereas in more concentrated acetone solutions (5–10%) the total amount of paramagnetic centres is constant during photolysis and the only product is CH_2COMe radicals. The difference observed in the behaviour of monomeric RC with increasing acetone concentration can be connected with more effective

Table 1 Spectral characteristics of acetone RC.

RC	λ_{max}, nm	$\varepsilon_{max}\times 10^{-3}$/dm^3 mol^{-1} cm^{-1}	f [a]
$Me_2CO^{+\cdot}$	$\simeq 435$	3.6 ± 0.6	$\simeq 0.10$
$(Me_2CO)_2^{+\cdot}$	$\simeq 715$	9.4 ± 1.2	$\simeq 0.25$

[a] The oscillator strength f was found from the equation $f = 4.32 \times 10^{-9}\ \varepsilon_{max}\ \Delta\nu_{1/2}$.

Table 2 Quantum yields (Φ) of photochemical reactions of acetone RC in the FM at 77 K.

RC	$\Phi_1 \times 10^2$	$\Phi_2 \times 10^3$	β [a]
$Me_2CO^{+\cdot}$	4.0 ± 1.0	4.0 ± 1.0	0.35 ± 0.05
$(Me_2CO)_2^{+\cdot}$	7.0 ± 2.0	20.0 ± 10.0	0.21 ± 0.08

[a] The proportion of RC with a relatively high reactivity (Φ_1).

charge transfer from the matrix RC to the acetone dimers (the ionization potential of dimers of polar compounds is significantly lower than for monomers) and their subsequent transformations.

$$Me_2CO^{+\cdot} \longrightarrow Me_2CO + FM^{+\cdot} \qquad (3)$$

$$FM^{+\cdot} + FM^{-\cdot} \longrightarrow 2\ FM \qquad (4)$$

$$FM^{+\cdot} + (Me_2CO)_2 \longrightarrow FM + (Me_2CO^{+\cdot})_2 \qquad (5)$$

Our results confirm that reactions (3) and (4) occur under the action of light on monomeric acetone RC. We have no proof of the occurrence of reaction (5) [we failed to see the absorption band ($D < 0.05$) belonging to dimeric acetone RC]; however, it should be taken into consideration in oder to explain the effects observed in the photolysis of monomeric acetone RC in concentrated solutions in FM. The small values of quantum yields (Table 2) of reaction (3) indicate a relatively low efficiency of charge-transfer to the matrix.

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Reference

1 T. Bally, in *Radical Ionic Systems*, eds. A. Lund and M. Shiotani, Kluwer Academic, Dordrecht, 1991, p. 3.

2 S. Arai, M. Hoshino and M. Imamura, *J. Phys. Chem.*, 1975, **79**, 702.

3 V. N. Belevsky, S. I. Belopushkin and V. I. Feldman, *J. Radioanal. Nucl. Chem. Lett.*, 1986, **107**, 81.

4 I. A. Leenson and G. B. Sergeev, *Dokl. Akad. Nauk SSSR*, 1972, **205**, 1400 (in Russian).

5 V. N. Belevsky and V. I. Feldman, *Radiochem. Radioanal. Lett.*, 1982, **51**, 121.

6 I. Yu. Tchapin, V. I. Feldman, V. N. Belevskii, I. A. Donskaya and N. D. Chuvylkin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 212 (*Russ. Chem. Bull.*, 1995, **44**, 1203).

7 P. J. Boon, L. Harris, M. T. Olm, J. L. Wyatt and M. C. R. Symons, *Chem. Phys. Lett.*, 1984, **106**, 408.

8 A. Kh. Vorob'ev and V. S. Gurman, *J. Photochem.*, 1982, **20**, 123.

9 K. Ushida and T. Shida, *Chem. Phys. Lett.*, 1984, **108**, 200.

10 A. Kira, M. Imamura, S. Tagawa and Y. Tabata, *Bull. Chem. Soc. Jpn*, 1986, **59**, 593.

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