Photochemical reactions of radical cations of dimethylformamide in freon matrices at 77 K

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Spectral characteristics of the radical cations (RC) of DMF ($\lambda_{max} = 415$ nm, $\varepsilon_{max} = (2.6\pm0.8) \cdot 10^3$ L mol⁻¹ cm⁻¹) stabilized in an irradiated glassy freon mixture (CFCl₃ and CF₂BrCF₂Br) at 77 K were determined. Amide type radicals and RC of the matrix were shown to be formed by irradiation ($\lambda = 365-436$ nm) of the radical cations of DMF in freon matrices using ESR and UV spectroscopy. The quantum yields of photoconversion of the DMF radical cations are independent of the wavelength of exciting light. It was found that the matrix structure affects the processes stabilizing the products of photoconversion of the DMF radical cations.

Key words: dimethylformamide, radical cations, freons, photochemical reactions, mechanism, quantum yields, absorption spectra. ESR.

Radical cations (RC) are active intermediates formed in various radiochemical, photochemical, catalytic, etc. processes. Because of the high reactivity of RC of various type in ion-molecular reactions, their properties and mechanisms of conversion are studied using the method of matrix isolation in freons at low temperatures.¹ Although it is well known² that the action of light causes conversions of RC, the mechanism of these conversions has been little studied. For many types of RC there is no information on their absorption spectra or on the quantum yields of their reactions or on the effect of the nature of the matrix and the photon energy on these reactions. Recently, we studied photochemical reactions of RC formed in various freons and in tetramethylurea³ and of monomeric and dimeric RC of acetone⁴ and first determined the quantum efficiency of these processes.

In this work, in a continuation of our studies, the photochemical reactions of the RC of dimethylformamide (DMF) and the effect of the nature of the freon matrix and the photon energy on the direction and efficiency of the processes have been investigated.

Experimental

Solutions of DMF (0.02-0.2 vol.%) in a mixture of freons (FM, freon-114B2 (CF₂BrCF₂Br) and freon-11 (CFCl₃)) (1 : 1 by volume) that was glassy at 77 K were dissolved in freon-11 or freon-113 (CF₂ClCFCl₂), evacuated to $\equiv 0.01$ Pa, and then exposed to X-ray irradiation (50 kV) with a dose of 0.5-2 kGy. The ESR and optical absorption spectra of the intermediates that formed were recorded on a Varian E-3 radio-spectrometer and a Specord M-40 spectrophotometer using the same samples with an optical path of 0.3 cm. A high-pressure mercury lamp (500 W) equipped with narrow-band glass filters

at $\lambda = 365 \text{ nm}$ ($T_{\text{max}} = 55\%$, $\Delta v_{1/2} \equiv 3100 \text{ cm}^{-1}$), $\lambda = 405 \text{ nm}$ ($T_{\text{max}} = 21\%$, $\Delta v_{1/2} \equiv 1700 \text{ cm}^{-1}$), and $\lambda = 436 \text{ nm}$ ($T_{\text{max}} = 36\%$, $\Delta v_{1/2} \equiv 2400 \text{ cm}^{-1}$) was used as the light source. The absolute light intensities were determined using ferrioxalate actinometry. The values of the extinction coefficients and quantum yields were averaged over five—six experiments, and the error for the confidence limit of 0.95 is indicated. The procedure for estimating the quantum yields of reactions of RC in polycrystalline freon-11 matrices was described in our previous work.³ Computer simulation of the ESR spectra of radical cations was performed using a program based on first-order perturbation theory, and only allowed transitions were taken into account.

Results and Discussion

Nearly identical signals were detected in the ESR spectra of solutions of DMF in all freons used that were irradiated at 77 K; the best resolution was reached in the matrix of freon-11. In accordance with the reported data,⁵ the ESR spectrum observed in this matrix was assigned to the RC of DMF (HCON(CH₃)₂^{.+}) due to the isotropic hyperfine structure (HFS) with $a_{\rm H}^{\rm iso} =$ 32.0 G from six equivalent protons; the small anisotropy of g-factor, $g_{\parallel} \approx 2.007$ and $g_{\perp} \approx 2.002$; and anisotropic HFS with $a_{\rm N,\parallel} =$ 38.6 G and $a_{\rm N,\perp} = 0$ from the nitrogen nuclei. The computer simulation of the ESR spectrum with the above parameters confirms the assignment of the observed signals to the RC of DMF.

Induced optical absorption in the $\lambda \le 800$ nm wavelength region is detected in the absorption spectra of irradiated solutions of DMF in FM at 77 K. A broad band in the 350-700 nm wavelength region of the absorption spectrum, which has been repeatedly ob-

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Fig. 1. Absorption spectrum of DMF RC in FM at 77 K.

served previously⁶ in irradiated FM and assigned to the absorption of the RC of freons, disappears after short-term irradiation with light of wavelength $\lambda \ge 680$ nm (in this case the concentration of the RC of DMF remains almost unchanged).

The subsequent action of light at λ 365, 405, and 436 nm on the RC of DMF in FM or freon-113 at 77 K results in changes in the ESR spectra, namely, a decrease in the intensity of the signal of the RC of DMF and the appearance of a poorly resolved triplet with splitting of ≈ 19.0 G and a g-factor close to 2.003 that was assigned to the $HCON(CH_3)CH_2$ radicals (the resolution of the spectrum is enhanced substantially with increased temperature). A parallel decrease in the intensity of the absorption band at $\lambda_{max} = 415 \text{ nm}$ (Fig. 1) occurs in the absorption spectra of irradiated glasses simultaneously with a decrease in the concentration of the RC of DMF detected by the ESR method. The observed parallelism made it possible not only to assign this band to the absorption of the RC of DMF, but also to determine the value of the extinction coefficient, $\varepsilon_{max} = (2.6 \pm 0.8) \cdot 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$, and the oscillator strength in the pertinent electron transition, $f \cong 0.06$.

It should be noted that an increase in the optical absorption in the shorter-wave region of the spectrum (Fig. 2) is observed simultaneously with the disappearance of the absorption band at $\lambda_{max} = 415$ nm, when the RC of DMF in FM are irradiated (for instance, by light at a wavelength of $\lambda = 405$ nm) at 77 K. According to the published data, the absorption band that appears at $\lambda_{max} \cong 370$ nm can be assigned either to absorption by the RC of freons $(\lambda_{max} = 360 \text{ nm})^{3,6}$ or to that by the radicals of DMF, HCON(CH₃)CH₂. Actually, the latter are known to have a fairly intense absorption band in the $\lambda \equiv 350-380$ nm region ($\epsilon \equiv$ $(1.6-2.5) \cdot 10^3$ L mol⁻¹ cm⁻¹).⁷ As can be seen from Fig. 2, the extinction coefficient of the intermediate formed in the photolysis of the RC of DMF is much larger than that of the latter. Investigations of the changes caused by the action of light at λ 365 nm in the intensities of the absorption band at $\lambda_{max} \cong 370$ nm and the signal of the DMF radicals in the ESR spectrum make it possible to assign the above band to the absorption of both the DMF radicals and the RC of freon-114B2,



Fig. 2. Differential absorption spectrum of irradiated solutions of DMF (0.02 vol.%) in FM photolyzed by light at a wavelength of 405 nm at 77 K.

 $CF_2BrCF_2Br^{+}$. Using the published data^{3,7} on the values of the extinction coefficients of the RC of freon-114B2 and the DMF radicals, it can be shown that in the case presented in Fig. 2 they are formed in a ratio close to 1 : 3.

Thus, the UV spectroscopy data show that photochemical reactions of the RC of DMF in a FM at 77 K result in the formation of both DMF radicals and the RC of freons. However, unlike the case of the RC of tetramethylurea (tmu) we studied previously,³ in this case we failed to experimentally detect the photoinduced transition of the RC of the freons to DMF RC. This can likely be associated with the low stationary concentration of the latter, which should have been expected because of the shift of the absorption band of the RC of DMF to a shorter-wave region of the spectrum than that of the RC of tmu ($\lambda_{max} = 513$ nm) and the possibility of mixed light absorption by the RC of freons and the RC of DMF under the experimental conditions.

A study of the kinetics of the decay of the RC of DMF by the ESR method made it possible to determine the quantum yields (Φ) of photochemical reactions of the RC of DMF in various matrices under the action of light at different wavelengths (λ 365, 405, and 436 nm) at 77 K.

Matrix	Ф ₃₆₅	Φ_{405}	Ф ₄₃₆
FM	0.3±0.15	0.2±0.1	0.25±0.1
Freon-11		≘0.3	≘0.4

As can be seen from these data, the quantum yields of the photochemical reactions have rather large absolute values and are virtually independent of the wavelength of the photolyzing light and the composition of the freon matrix.

At the same time, the kinetics of photoconversions of the RC of DMF appeared to be extremely sensitive to the structure of the matrices used. Thus, the photoconversions of the RC of DMF in glassy freon-113 and FM matrices result in the formation of DMF radicals



Fig. 3. The kinetics of conversion of the RC of DMF under the action of light at a wavelength of 405 nm at 77 K in FM (a) and freon-11 (b): I, changes in the concentration of the RC of DMF; 2, changes in the total concentration of paramagnetic species.

and occur without changing the total concentration of the paramagnetic species. Photolysis in a polycrystalline matrix of freon-11 also results in the formation of DMF radicals, but is accompanied by an appreciable (more than twofold) decrease in the concentration of paramagnetic species (Fig. 3) as a result of the photostimulated recombination of the RC of DMF with the radical anions of freon. In this case, the results we obtained exhibit no correlation between the efficiency of photorecombination and the excess energy obtained by the RC of the matrix in this process (ionization potentials (1) are equal to 11.99 (freon-113); 11.77 (freon-11); 11.44 (freon-114B2), and 9.12 eV (DMF); the energies of the photons at λ 365, 405, and 436 nm are equal to 3.4, 3.06, and 2.84 eV, respectively). The observed differences in the kinetics of photoconversions of the RC of DMF in various freons (glassy and polycrystalline) indicate that the mechanisms of the migration of the "holes" in these matrices are different.

Thus, the results of our work show that the radical cations of DMF in freon matrices undergo conversions of two basic types under the action of light:

1. DMF radicals form, most likely as a result of photoisomerization of the RC of DMF (as was shown previously,⁵ thermal ion-molecular reactions can not proceed at 77 K at the concentrations of the DMF solutions we used)

 $HCON(CH_3)_2^{++} \Rightarrow HC(OH)^+N(CH_3)CH_2^+;$

2. RC of freons form as a result of abstraction of an electron from the matrix molecules by the excited RC of DMF

 $\mathrm{HCON}(\mathrm{CH}_3)_2^{+} + \mathrm{M} \Rightarrow \mathrm{HCON}(\mathrm{CH}_3)_2 + \mathrm{M}^{+}.$

It is important to note that the pathways of the photoconversion of the RC of DMF in solid freon matrices differ substantially from the fragmentation processes known for excited RC of DMF obtained by the field ionization technique.⁸

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