Spectral features of 1,2-biradicals isomeric to C_2—C_4 perfluoroolefins

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Absorption spectra of 1,2-biradicals were obtained by kinetic spectroscopy under adiabatic compression of mixtures of perfluoroolefins with argon.

Key words: biradicals, UV spectra, adiabatic compression.

In the last 10—15 years, formation of various biradical structures has been reliably established in thermal and photochemical reactions (see Refs. 1 and 2), and their spectral data have been obtained. All of these species are "separated" biradicals in which the atoms bearing unpaired electrons are not directly bound to one another.

Only recently theoretical views of the possibility of existence of singlet 1,2-biradicals have been experimentally confirmed.[3,4] It was found that the enthalpy of the reaction

$$C_2F_4 \rightleftharpoons C^{\cdot}F_2—C^{\cdot}F_2 \qquad (1)$$

is only 18±2 kcal mol^{-1}.

The purpose of the present study is to obtain spectral characteristics of the 1,2-biradicals formed from perfluoroolefins when they are heated under strictly homogeneous conditions.

The spectra were measured using the previously described setup.[3] Mixtures of extra pure argon with perfluoroolefins, C_2F_4, C_3F_6, 1-C_4F_8, or 2-C_4F_8, with proportions of the latter of 1—10 % (v/v) were adiabatically compressed.

With each mixture, we carried out a series of runs whose conditions were identical within the experimental error. In each run we obtained the time dependence of light absorption at a certain individual wavelength. The adiabatic heating was carried out to temperatures at which CF_2 cannot be spectrally detected.

We found that the time dependences of the light absorption are cupola-shaped curves, symmetrical about the instant at which the maximum temperature and pressure are attained. A symmetrical curve is possible only in the case where an equilibrium between perfluoroolefins and the corresponding 1,2-biradicals is achieved. The concentration of the latter is governed by the equilibrium constant of reversible cleavage of the π-bond in perfluoroolefins (reaction (1)).

The thermal effect of the reaction and the product of the preexponential factor of the equilibrium constant of this process by the extinction coefficient were determined by mathematical simulation in the processing of the experimental results. By comparing the data on the absorption of light by mixtures with various proportions of one particular perfluoroolefin, extinction coefficients of 1,2-biradicals were evaluated.

Figure 1 presents the experimental data on the absorption of light by various 1,2-biradicals in the $220 < \lambda < 260$ nm range. The lines that connect experimental points in Fig. 1 were drawn by the method of third-order spline functions; the extinction coefficients of 1,2-biradicals at the maxima of their absorption bands are also presented in this figure.

The enthalpies of reaction (1) found by mathematical simulation and the extinction coefficients at the maxima of absorption bands coincide to within the experimental and calculation errors in all of the cases studied. This is evidence in support of the view that the natures of all of the intermediates are identical.

A comparison of the data presented in Fig. 1 makes it possible to conclude that the maxima of the absorption bands of the biradicals derived from perfluoro-α-olefins shift to the long-wave region as the molecular weights of these biradicals increase. In fact, for the $C^{\cdot}F_2—C^{\cdot}F_2$ biradical, $\lambda_{max} \approx 236.5$ nm, for $CF_3—C^{\cdot}F—C^{\cdot}F_2$, $\lambda_{max} \approx 240$ nm, and for $CF_3—CF_2—C^{\cdot}F—C^{\cdot}F_2$, $\lambda_{max} \approx 242.5$ nm.

For all of the type (1) reactions, conditions exist in which no intermediates (except for 1,2-biradicals) are detected by spectroscopy and no stable products are found by chromatography. Formation of the 1,2-biradical from perfluoro-2-butene is an exception, since it is accompanied by *cis-trans*-isomerization. It is likely that after the $CF_3—C^{\cdot}F—C^{\cdot}F—CF_3$ biradical is formed rotation around the central C—C bond becomes possible.

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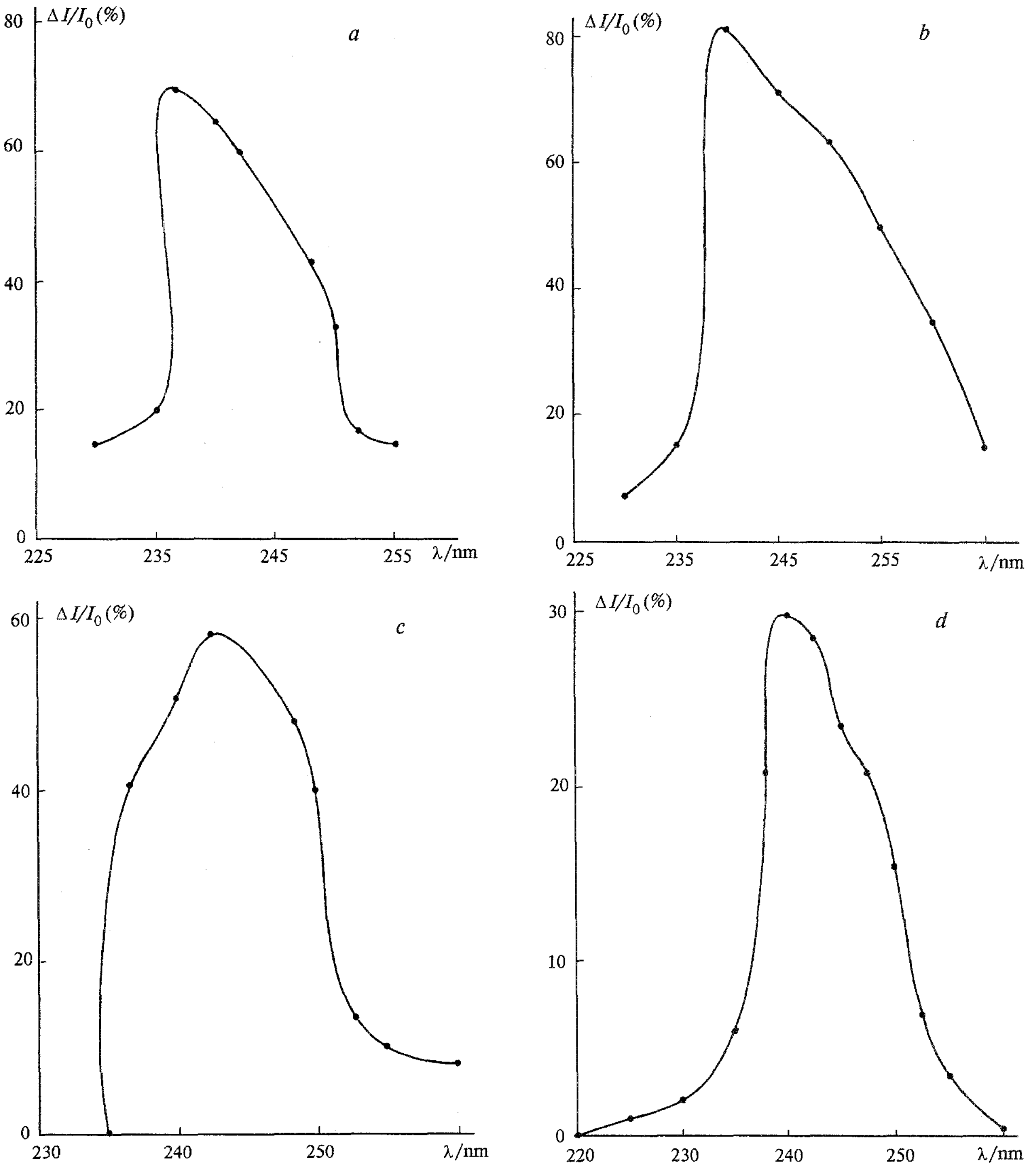

Fig. 1. Absorption spectra of 1,2-biradicals (adiabatic compression of mixtures of C_2—C_4 perfluoroolefins with argon); the size of the points corresponds to the error of the measurements (σ/cm^2 mol^{-1} is the extinction coefficient): 10% (v/v) C_2F_4, T_{max} = 890 K, σ (λ = 236.5 nm) = $(6\pm1.0)\cdot10^6$ (*a*); 1% (v/v) C_3F_6, T_{max} = 1233 K, σ (λ = 240 nm) = $(3.5\pm0.5)\cdot10^6$ (*b*); 1.2 % (v/v) 1-C_4F_8, T_{max} = 1010 K, σ (λ = 242.5 nm) = $(3.5\pm0.5)\cdot10^6$ (*c*); 1.5 % (v/v) 2-C_4F_8, T_{max} = 1113 K, σ (λ = 240 nm) = $(3.8\pm0.5)\cdot10^6$ (*d*).

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