

Photochemical separation of isotope by the isotope-trap method

R. Z. Sagdeev, S. V. Kamysan, A. A. Obynochnyĭ, and Yu. N. Molin

Institute of Chemical Kinetics and Combustion, Siberian Division, USSR Academy of Sciences

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An isotope-separation method is proposed, based on isotopic effects in the transfer of electron excitation at low temperatures. An experimental separation coefficient of 88 was obtained for the isotopes H and D in a mixture of H₄- and D₄-acetaldehyde.

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The existence of isotopic effect in the transfer of energy in crystals at low temperatures is a well known fact.^[1,2] These effects were observed in the study of luminescence in crystals with isotopic impurities. Owing to the difference between the energy of the electronic excitation of molecules with different isotopic compositions, some of them take on at low temperatures the role of isotopic energy traps, and this manifests itself in a preferred emission of such molecules.

In this paper we propose to use the difference between the excitation energies of isotopically-substituted molecules to separate isotopes photochemically. For the proposed method it is necessary to satisfy the following conditions: 1) The temperature at which the photolysis is carried out satisfies the relation $kT < \Delta E$, where ΔE is the depth of the trap. 2) The excitation-energy transfer between the isotopic molecules must be faster than the photochemical transformation. In addition, it is desirable to have the quantum yield of the decomposition close to unity.

The proposed method was verified experimentally, using as an example the separation of the isotopes H and D in mixtures of the acetaldehydes CH₃COH and CD₃COD. The chosen system satisfies all the foregoing conditions. The photolysis of the mixtures of acetaldehydes, with the oxygen pumped out, was carried in quartz ampoules (working-part diameter 3 mm) in the full light of a DRSh-500 mercury lamp at liquid-nitrogen and liquid-helium temperatures. For comparison, photolysis was carried out of mixtures of acetaldehyde in the liquid state ($T = 273^\circ\text{K}$). The main products of the photolysis of the acetaldehyde are methane, carbon monoxide, and formaldehyde. Their analysis was carried out with MKh-1303 and MS-3301 mass spectrometers. According to the published data,^[3] the photodecomposition of acetaldehyde in the region of the $n-\pi^*$ transitions proceeds mainly along two paths:



The second path becomes significant at short wavelengths. The methyl radicals produced in the reaction (1) from H₄-acetaldehyde in the mixtures can yield both CH₄ and CH₃D. Thus, the degree of decomposition of the H₄-acetaldehydes must be characterized by the combined amount of the methanes CH₄ and CH₃D. Similarly, the degree of decomposition of the D₄-acetaldehyde

is determined by the total amount of CH₄ and CD₃H.

The table gives the ratios of the methane concentrations in a 1:1 mixture of H₄ and D₄ acetaldehydes, observed after photolysis at three temperatures.

| Temperature, °K | Isotopic effect |
|-------------------|-----------------|
| 273 | 1.9 |
| 77 | 10.4 |
| 4.2 ¹⁾ | 88.0 |

The results show that the normal acetaldehyde is decomposed in the mixture at a faster rate. The magnitude of the H-D isotopic effect increases with decreasing temperature, reaching a value 88. An isotopic effect of order 10-20, was obtained by us also from observations of the EPR spectra of the methyl radicals CH₃ and CD₃ in the photolysis of the same acetaldehyde mixture at 77°K. The character and scale of the observed isotopic effect are in full agreement with the general idea of the isotopic traps. Indeed, in this case, the H₄ acetaldehyde assumes the role of the isotopic trap, and the depth of the trap is²⁾ $\sim 120 \text{ cm}^{-1}$. The distribution of the excitation energy among the isotopic modifications of the molecules (at rapid energy transfer) should be determined by the Boltzmann factor $\exp(-\Delta E/kT)$. It is then easy to estimate that the foregoing value of ΔE at 77°K should correspond to an isotopic effect ~ 10 .

Additional proof that the observed isotopic effect is connected with capture of the electron-excitation energy by the molecules of the H₄-acetaldehyde was obtained by us by investigating the photolysis of a 1:1 mixture of acetaldehydes diluted with heavy water in a ratio 1:1000 at $T = 77^\circ\text{K}$ (we added ZnCl₂ to the water to obtain glasses). In this case we were unable to observe the isotopic effects from the products

$$\frac{[\text{CH}_4 + [\text{CH}_3\text{D}]]}{[\text{CD}_4] + [\text{CD}_3\text{H}]}$$

nor from the EPR spectra of the methyl radicals. The last result becomes understandable if it is assumed that the photochemical decomposition of the acetaldehyde occurs mainly from the triplet state. It is known that the transfer of the triplet energy in the condensed phase proceeds via an exchange mechanism that is effective only at short distances (i.e., at large concentrations).^[5]

Thus, our experiments show that isotopic effects in

themselves in photochemical reactions and can be used to separate the hydrogen isotopes.

An analysis of the published data on the values of ΔE (from the values of the isotopic shifts for the 0-0 band in the electronic spectra^[6]) shows that at helium temperatures the proposed method can be used to separate also other isotopes. Thus, for example, for molecules containing the isotopes B¹⁰ and B¹¹ the value of ΔE reaches $\sim 20 \text{ cm}^{-1}$, which is appreciably more than the value of kT at helium temperatures ($\sim 3 \text{ cm}^{-1}$).

¹⁾Inasmuch as the photolysis at helium temperatures was carried out without a thermal filter, there are grounds for assum-

ing that the temperature in the reaction zone exceeded 4.2°K somewhat.

²⁾We succeeded in obtaining the value of ΔE for the related compound formaldehyde: $\Delta E \sim 120 \text{ cm}^{-1}$.^[4]

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