LIFETIME OF NEGATIVE MOLECULAR IONS FORMED IN SEVERAL RESONANCES AT SUBTHERMAL ENERGIES

O. A. Ponomarev and V. A. Mazunov

UDC 541.124.7:539.124:547.556.3

Long-lived mass-spectrometrically observed molecular ions have lifetimes in the micro- to millisecond range [1]. This is so great a time for the relaxation processes that any redistribution of the excess energy among the degrees of freedom is possible, since the geometry of the molecular system can change during times on the order of 10^{-13} to 10^{-12} sec.

As a rule, the geometries of stable singly charged negative ions and molecules are different. Therefore, the ions are often fairly stable with respect to the ejection of an electron into the continuous spectrum. During a relaxation process taking place after electron capture, various conformational changes which prevent the ejection of an electron back into the continuous spectrum are possible. This probability is determined by the structure of the molecule and the nature of the interactions which result in the redistribution of the energy.

The purpose of the present work was to ascertain the mechanisms of the relaxation process by evaluating the lifetime of negative molecular ions formed as a result of the capture of electrons by means of different resonances with similar energies. The solution of the problem posed required the preliminary revelation of classes of molecules of the same structure, which are characterized by the existence of several resonances, rather than the addition of several new members to a known "motley" list of molecules [1]. Two classes of compounds (substituted azo- and azoxybenzenes), whose molecules capture electrons by a nondissociative mechanism in the 0-1-eV energy range in more than one resonance process, were discovered. The features of the resonance for the compounds under investigation were found to be associated with the existence of two (or several) isomeric forms of the original molecules. The utilization of theoretical and experimental methods of investigation made it possible to relate the number of resonances and the lifetimes of the ions (with respect to the autoejection of an electron) τ in each of them to the structure of the molecules, the temperature, and the energy of the bombarding electrons.

The negative molecular ions of complex molecules (M^-) are metastable, and, unless they are specially stabilized, they subsequently decompose into a neutral molecule and an electron. The value of the lifetime $\tau(M^-)$ and its dependence on the energy of the electrons within the resonance were measured for each type of molecular ion. The closely positioned peaks of M^- were resolved by the method described in [2]. The temperature dependence of the lifetime $\tau(M^-)$ of the ions obtained by capture in different subthermal resonances was investigated.

It was found that the lifetime of the first resonance peak τ_1 ($E_1 \cong 0$ eV) is always greater than (or equal to) the lifetime τ_2 of the ions obtained by capture in a resonance with a greater energy. In all cases, the value of τ_2 decreases within the resonance as the energy of the electrons is increased. At the same time, τ_1 either remains unchanged or also decreases. The results obtained are presented in Table 1.

The dissociation of the ions occurs as a result of fluctuations, during which the energy is redistributed in such a manner that the system returns to its original state. It should be kept in mind that not all the energy of the electron is converted into internal energy of the ion and that some of it is utilized to alter the translational and rotational energies of the molecule. Estimates show that this portion of the energy is not very significant and amounts to from 10 to 30% of the kinetic energy of the electron. This redistribution of the energy will be taken into account with the aid of the energy-transfer parameter α.

When the processes resulting in the dissociation of ions are considered, it is usually assumed that the energy obtained by an ion from the kinetic energy of the bombarding electron (E) and the electron affinity with respect to the first isomer (U_1) is distributed

---

Department of Physics and Mathematics, Academy of Sciences of the USSR, Bashkir Branch, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 347-352, February, 1986. Original article submitted September 24, 1984.

0568-5230/86/3502-0320$12.50

TABLE 1. Positions of the Maxima of the Resonances and Lifetimes of Negative Molecular Ions of Azobenzenes and Azoxybenzenes at 350°K

Compound	E_m,	τ, μsec		
		experiment (plus/minus 10 percent)	calculation acc. to Eq. (7)	acc. to Eq. (9)
$C_6H_5N{=}NC_6H_5$	0	40	40	100
	0,95	24	1,2	1,2
m-$NH_2C_6H_4N{=}NC_6H_5$	0		$4 \cdot 10^6$	2000
	1,1	20	20	5
p-$NH_2C_6H_4N{=}NC_6H_5$	0	180	–	100
p-$FC_6H_4N{=}NC_6H_5$	0	–	10^8	2000
	1,1	100	100	5
p-$ClC_6H_4N{=}NC_6H_5$	0	–	1000	800
	0,5	200	200	30
m-$ClC_6H_4N{=}NC_6H_5$	0	500	500	800
	0,5	200	80	30
o-$ClC_6H_4N{=}NC_6H_4Cl$-o	0	800	800	800
	0,5	150	80	30
	0,7	–	24	10
2-OH, 4-$Cl{=}C_6C_3N{=}NC_6H_5$	0	5000	5000	2000
	0,4	2000	600	130
	0,6	150	150	80
	0,9	–	40	15
p-$CH_3C_6H_4N{=}NC_6H_4Cl$-p	0	400	400	800
	0,4	110	40	30
p-$BrC_6H_4N{=}NC_6H_5$	0	70	70	100
	0,4	70	7	10
p-$BrC_6H_4N{=}NC_6H_4Br$-p	0	240	–	100
m-$NO_2C_6H_4N{=}NC_6H_5$	0	–	2600	2000
	0,9	–	150	20
	1,5	70	70	2,5
p-$NO_2C_6H_4N{=}NC_6H_5$	0	1600	1600	2000
	0,6	–	285	80
$C_6H_5N{=}N(O)C_6H_5$	0	440	440	800
	0,6	44	32	30
$C_6H_5N{=}N(O)C_6H_4Br$-m	0	300	–	800
$C_6H_5N{=}N(O)C_6H_4NO_2$-m	0	2500	2500	2000
	0,6	450	300	80

evenly among all the degrees of freedom. The existence of several resonances permits the experimental verification of this hypothesis.

In the case of uniform distribution of the energy among all the degrees of freedom, the lifetime of M^- depends on the energy corresponding to one degree of freedom, i.e., on the temperature of the ion:

$$\tau = f\left(\frac{U_1}{n} + kT + \frac{\alpha E}{n}\right) \tag{1}$$

where n is the number of degrees of freedom, and kT corresponds to the temperature of the molecule before electron capture. If the redistribution of the energy involves less than all the degrees of freedom, the value of n should be replaced by the effective number of degrees of freedom n^* ($n^* < n$). Then the formula for τ takes on the form

$$\tau = f\left(\frac{U_1}{n^*} + kT + \frac{\alpha E}{n^*}\right) \tag{2}$$

From Eqs. (1) and (2) it follows that the changes in the lifetime upon the changes in kT and $\alpha E/n^*$ by the same quantity should be identical. This permits the determination of n^*, since U_1, kT, and E can be determined experimentally. In the case of N-phenylpyromellitimide at 80°C, $n^*kT + U_1 \approx 5$ eV, and as the energy was increased, continuously decreasing lifetimes were observed with increasing energies of the resonances: $\tau_1 \cong 1200$ sec, τ_2 (1 eV) = 600, τ_3 (2 eV) = 300, τ_4 (3 eV) = 70 μsec [3]. In this case, it was experimentally established that

$$f\,(U_1/n^* + 0.028 + 0.4\alpha/n^*) = 750 \ \mu\text{sec}$$
$$f\,(U_1/n^* + 0.047 + 0.42\alpha/n^*) = 200 \ \mu\text{sec}$$
$$f\,(U_1/n^* + 0.028 + 0.92\alpha/n^*) = 196 \ \mu\text{sec}$$

Hence it follows that

$$U_1/n^* + 0.047 + 0.42\alpha/n^* \approx U_1/n^* + 0.028 + 0.92\alpha/n^* \text{ and } n^* \approx 33$$

The total number of vibrational degrees of freedom for this molecule n = 111. Even if $\alpha \not\gtrsim 1$, ∿30% of the degrees of freedom, among which the energy is distributed evenly, participate in the redistribution of the energy. The remaining ∿70% of the degrees of freedom are not active in the millisecond range. This result was obtained under the single assumption that the energy is evenly distributed among the active degrees of freedom without the use of an explicit form for the function $\tau(M^-)$ and, in this sense, is general. The conclusion that not all the degrees of freedom are equally active in the energy-relaxation processes is supported by other investigations [4].

Let us next obtain the explicit form of the function $\tau(M^-)$. For this purpose we shall use the Franck–Condon model of electron capture by a molecule. Regardless of the resonance in which the electron is captured, the dissociation of the ion generally involves the isomer with the lowest energy (which will be designated as the first isomer below). The lifetime with respect to autoejection of an electron for this model can be determined with the use of the formula [5]

$$\tau = \left[\int_0^\infty W(E')\,\rho(E')\,dE'\right]^{-1} \tag{3}$$

where $\rho(E') = \Sigma\delta(E - k\omega)$, ω is the effective vibrational frequency of the ion, and $W(E')$ is the probability of a transition from the state of an ion to the state of a molecule plus an electron. For the calculation of the transition probability $W(E')$ we shall take advantage of its representation in terms of a correlation function of fluxes. In the case of the scheme of levels in Fig. 1, the dynamics of the system, which describes the transition probability, can be calculated, if we choose the Hamiltonian

$$H = H_1(Q)\,a_1{}^+a_1 + \Sigma H_{pk}(Q)\,a_p{}^+a_k + \Sigma V_{1p}\,(a_1{}^+a_p + a_p{}^+a_1) \tag{4}$$

where $a_i{}^+$ denotes the creation operators of an electronic state in the initial term (i = 1) or in the state of an isomer p. Here

$$H_1(Q) = \Sigma\omega_q b_q{}^+b_q + \Sigma A_q(b_q + b_q{}^+) + \Sigma F_{qq_1}(b_q + b_q{}^+)(b_{q_1} + b_{q_1}{}^+)$$
$$H_{pp}(Q) = \sum\omega_{pq}b_q{}^+b_q + \sum A_{pq}^{(2)}(b_q + b_q{}^+) + E_pE'$$
$$H_{pq}(Q) = I_{pq},\quad p \neq q;$$

$b_q{}^+(b_q)$ denotes the creation (annihilation) operators of the vibrational states with a frequency ω_q; A_q, F_{qq}, and I_{pq} are parameters.

The probability of a transition to the p-th minimum is determined by the value of

$$G(t) = \langle a_1{}^+(0)\,a_p(0)\,a_p{}^+(t)\,a_1(t)\rangle$$

where the averaging <...> is carried out over a Gibbs distribution with the Hamiltonian H_1. The transition probability is expressed by the formula

$$W(E) \sim \operatorname{Re}\int_0^\infty dt G(t)$$

We calculated the value of G(t) in [6] for a Hamiltonian of type (4). After integration we have

$$\tau \sim \frac{B_1}{\sqrt{2\pi}}\exp\left\{\frac{[E_2 - E_1 - k\omega + 2\Sigma(A_q{}')^2/\omega_q + \Sigma F_{qq}(2N_q + 1)]^2}{2B_1{}^2}\right\}. \tag{5}$$

where

$$B_1{}^2 = \Sigma(A_q{}')^2(2N_q + 1) + 2\Sigma F_{qq_1}^2(2N_q + 1)(2N_{q_1} + 1)$$
$$A_q{}^1 = (A_{1q}^{(2)} - A_p),\quad N_q = (e^{+\omega_q/kT} - 1)^{-1}$$

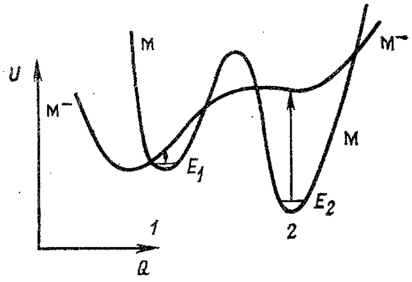

Fig. 1

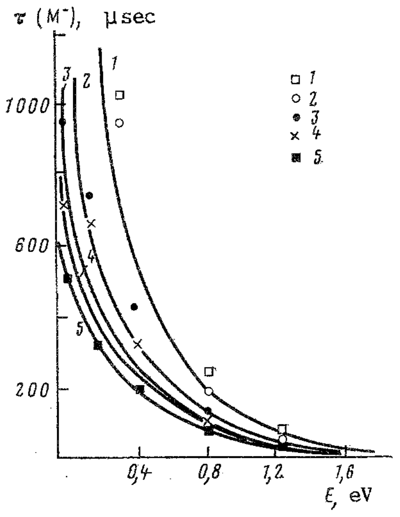

Fig. 2

Fig. 1. Scheme of the potential surfaces of a negative molecular ion.

Fig. 2. Dependence of the lifetime $\tau(M^-)$ on the energy of electrons for p-nitroazobenzene (the points represent experimental values, and the solid curves represent theoretical calculations) at the temperatures, °C: 1) 60; 2) 80; 3) 195; 4) 235; 5) 275.

The temperature change due to the supply of energy from without (E) and the electron affinity measured from the p-th isomeric state (U_p) was taken into account in this expression, and instead of the temperature of the molecule kT, the ion has the temperature $kT + (\alpha E + U_p)/n^*$. If we neglect the small correction associated with the frequency effect, we have

$$\ln\tau \sim \ln A + \frac{[U_1 - k\omega + 2\Sigma (A_q^1)^2/\omega_q]^2}{2\Sigma (A_q^1)^2(2N_q + 1)} \tag{6}$$

We take into account the fact that dissociation takes place mainly from a state with k = 0, and we introduce the effective filling number of the vibrational states N of the negative molecular ions as defined in the reaction

$$\Sigma\,(A_q^1)^2(2N_q + 1) \approx (2N + 1)\,\Sigma\,(A_q^1)^2$$

Next, taking into account that ln A is weakly dependent on E and T, we obtain

$$\tau(E) = A\,(\tau_0/A)^{(N(0)+0.5)\,(N(E)+0.5)^{-1}} \tag{7}$$

where $\tau_0 = \tau(E = 0)$, and $N(0) = N(E = 0)$. The value of τ_0 depends on the temperature:

$$\tau_0(kT) = A\,(\tau_0(kT_0)/A)^{(N_0+0.5)\,(N(0)+0.5)^{-1}} \tag{8}$$

where $N_0 = N(E = 0, kT = kT_0)$. The use of Eqs. (7) and (8) for the calculation of the relative lifetime of ions is convenient, since the unknown resonance integral, which varies from molecule to molecule, has been replaced by the measurable parameter τ_0.

For the calculation of the lifetime, we take $\alpha \approx 0.7$ and ω = 500-1000 cm^{-1} (0.05-0.10 eV). The electron affinity for the molecules under consideration is ∿0.5 eV, and the number of internal degrees of freedom is easily calculated. The value of A is determined from the lifetime following capture in one of the resonances. For example, in the case of p-nitroazobenzene, the value of A determined from the lifetime at an energy of 1.6 eV and T = 333°K was found to be equal to $4 \cdot 10^{-5}$ μsec. This value was adopted for all the nitroazobenzenes, since the capture of an electron by the molecules of these compounds occurs at the nitro group, and the resonance parameter for them is, therefore, probably approximately the same. The results of the calculation of the lifetime on the basis of Eq. (7) with $A = 4 \cdot 10^{-5}$ μsec and the value of τ_0 determined with E = 0 for the nitro-substituted derivatives are presented in Table 1. For the remaining derivatives of azobenzene it was assumed that $A = 10^{-4}$ μsec. The value $A = 10^{-4}$ μsec was also taken for the azoxybenzenes (without an NO_2 group), and the value $A = 4 \cdot 10^{-5}$ μsec was taken for the nitro derivatives. The results of the calculations for these compounds are also presented in Table 1. The agreement with the experiment proved to be adequate.

Expression (7) does not reveal the relationship between the characteristics of a molecule and the lifetime of its negative molecular ion to a sufficient degree. We shall, therefore, consider expression (5), in which this relationship is explicitly expressed, in greater detail. For the calculation of the lifetime with the use of formula (5), we shall use the value of A determined above, since it is governed mainly by the resonance integral and is identical for a class of molecules. In the case of high temperatures, after the introduction of the effective frequencies we have

$$\Sigma\,(A_q^1)^2/\omega_q = \Delta^2/\omega \quad \Sigma\,(A_q')^2(2N_q+1) = 2\Delta^2\,(kT)/\omega$$

Now

$$\ln\tau = \ln A + \frac{\left(\frac{U_1}{\omega} + 2\Delta^2/\omega^2\right)^2 \omega}{4\,(\Delta^2/\omega^2)\,(kT + (\alpha E + U_p)/n^*)} \qquad (9)$$

This equation contains two unknown parameters: ω and Δ. The value of ω can be estimated from the value of the energy of the active vibrations and lies in the range from 500 to 1500 cm^{-1}. The value of Δ/ω is determined independently from the width of the effective capture cross section. For the molecules under consideration it is equal to 3-4. For the calculation we take $\omega = 0.1$ eV and $(\Delta/\omega) = 3.5$. The values of Δ and ω should be chosen by a more rigorous approach for each molecule. This was, in fact, done in (7). The use of (9) requires the identification of a class of molecules with close values of ω and Δ. The list of compounds presented in Table 1 may be subdivided into three classes: molecules with τ_0 = 100, 800, and 2000 μsec. Selecting the value of Δ/ω for these classes and carrying out the calculations with the use of Eq. (9), we obtain the results presented in Table 1. These results are in poorer agreement with the experiment than are those obtained with the use of Eq. (7), in which the individual properties of the molecules are taken into account more accurately. Expression (9) can, therefore, be used only to estimate the lifetime. However, expression (8) has preference over Eq. (7), since it explicitly points out the relationship of the lifetime of an ion to the structure and characteristics of molecules.

From the dependence of the lifetime on the energy for p-nitroazobenzene (Fig. 2) it is seen that at small energies the theoretical dependence of τ on E is stronger than that observed experimentally. However, beginning at 0.8 eV, the agreement between the theory and the experiment is good. As the temperature is increased, the agreement between the theory and the experiment improves, and at 275°C the theoretical and experimental curves practically coincide. In the case of the N-phenylpyromellitimide molecule, the temperature may be assumed to be high. Then

$$\tau\,(E) = A\,(\tau_0/A)^\gamma \qquad (10)$$

where

$$\gamma = (n^*kT + U_1)/(n^*kT + U_1 + \alpha E).$$

At 80°C $n^*kT + U_1 \approx 5$ eV, and $A \approx 1$ μsec. A calculation based on Eq. (10) showed that τ(0) = 2000 μsec, τ (1 eV) = 790, τ (2 eV) = 378, and τ (3 eV) = 130 μsec; the corresponding values are equal to 1200, 600, 300, and 70 μsec [3]. Thus, the theory is in sufficiently good agreement with the experiment, confirming the correctness of the assignment of the compound resonances to different isomeric forms of the original molecule.

CONCLUSIONS

1. The lifetimes with respect to the autoejection of an electron for negative molecular ions in binary and more complicated resonances and their dependence on the energy have been measured for 16 azo- and azoxybenzene derivatives.

2. The relation of the lifetime to the displacement of the terms, the frequencies of the active vibrations, and other characteristics of the molecule has been established.

3. Only some of the vibrational degrees of freedom participate in the process of the relaxation of the energy in negative molecular ions during times shorter than 10^{-6} sec.

LITERATURE CITED

1. V. I. Khvostenko, V. A. Mazunov, and B. G. Zykov, in: Mass Spectrometry of the Resonance Capture of Electrons and Photoelectron Spectroscopy [in Russian], BFAN SSSR, Ufa (1983), Part 9.
2. V. A. Mazunov, V. I. Khvostenko, V. S. Fal'ko, and V. Sh. Chanbarisov, Izv. Akad. Nauk SSSR, Ser. Khim., 2383 (1981).
3. C. D. Cooper and R. N. Compton, J. Chem. Phys., 59, No. 10, 3550 (1973).
4. V. I. Khvostenko, Mass Spectrometry of Negative Ions in Organic Chemistry [in Russian], Nauka, Moscow (1981).
5. A. I. Ivanov and O. A. Ponomarev, Izv. Akad. Nauk SSSR, Ser. Khim., 2493 (1976).
6. A. I. Ivanov, G. S. Lomakin, and O. A. Ponomarev, Teor. Mat. Fiz., 41, No. 2, 209 (1979).

PREPARATION AND REACTIVITY OF METAL-CONTAINING MONOMERS. COMMUNICATION 4. RADIATION-INDUCED GRAFT POLYMERIZATION OF ACRYLAMIDE COMPLEXES OF Co(II), Ni(II), AND Cu(II) ON POLYETHYLENE

V. S. Savost'yanov, A. D. Pomogailo,
D. A. Kritskaya, and A. N. Ponomarev

UDC 541.15:541.64:541.49

An investigation of radiation-induced graft polymerization on polyethylene (PE) powder of Co(II), Ni(II), and Cu(II) acrylates – metal-containing monomers (MCM) with a metal σ bond – showed that introduction of a metal into the monomer molecule significantly changes the kinetics of the process [1]. It was also shown [2] that donor–acceptor bonding of an allyl monomer (allyl alcohol) to a transition-metal compound significantly accelerates the process of graft polymerization on PE.

The purpose of the present paper is an investigation of graft polymerization of MCM with donor–acceptor metal bonds, namely, acrylamide (AA) complexes of Co(II), Ni(II), and Cu(II), on preliminary γ-irradiated PE and comparison of the main parameters of the process with grafting of AA and other acrylic monomers.

EXPERIMENTAL

Acrylamide complexes of Co(II), Ni(II), and CU(II) were obtained according to [3] and [4]. Elemental analysis confirmed their composition: $CoCl_2 \cdot 4AA$, $Co(NO_3)_2 \cdot 4AA$, $NiCl_2 \cdot 4AA$, and $CuCl_2 \cdot 4AA$ (Table 1). The procedure for carrying out graft postpolymerization of MCM on PE powder and the analysis of the obtained graft copolymers were the same as in [1].

TABLE 1. Elemental Composition of Acrylamide Complexes of Co(II), Ni(II), and Cu(II)

Complex	Found, percent					Calculated, percent					
	C	H	N	Cl	M	C	H	N	Cl	O	M
$CoCl_2 \cdot 4AA$ (I)	36,2	5,3	13,6	17,4	12,8	34,8	4,8	13,5	17,1	15,5	14,2
$Co(NO_3)_2 \cdot 4AA$ (II)	29,6	5,0		—	11,5	30,8	4,3	18,0	—	34,2	12,6
$NiCl_2 \cdot 4AA$ (III)	34,9	5,2	17,1	13,4	14,0	34,8	4,8	13,5	17,1	15,5	14,2
$CuCl_2 \cdot 4AA$ (IV)	34,6	4,9	13,7	15,0	13,9	34,4	4,8	13,4	16,9	15,3	15,2

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 353-356, February, 1986. Original article submitted August 3, 1984.