a second electrostatic analyzer (ESA-II). The field-free regions (FFR), located between the source and ESA-I (1st FFR), and between the magnet and ESA-II (3rd FFR), are equipped with standard collision cells. An Ion Tech saddle-field atom gun (Ion Tech, Middlesex, England) was used for producing 7-to 8-keV Ar atoms for FAB desorption in a commercially available Kratos FAB source.

For FAB-MS/MS experiments, an ion of interest was selected by using MS-I at a mass resolution of approximately 1000 (width at 10% height). Mass selected ion kinetic energy spectra (MIKES) were obtained by scanning MS-II. Twenty scans were averaged using software written in this laboratory. CA experiments were done by activating the mass selected ion in the third FFR by using a helium pressure that gave a 50% main beam suppression.

For MS/MS/MS experiments, source-produced ions were activated in the first field-free region. The fragment ion of interest was then transmitted to the third FFR by setting both the first ESA and the magnet at the appropriate values. The selected daughter ion was collisionally activated and the resultant second generation fragment ions were analyzed by scanning the final electric sector.[29]

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An Algorithm for the Design of Propagating Acidity Fronts

Lajos Szirovicza, István Nagypál,* and Endre Boga

Contribution from the Institute of General and Physical Chemistry, Attila József University, H-6701 Szeged, P.O. Box 105, Hungary. *Received June 13, 1988*

Abstract: On the basis of elementary chemical considerations, it is shown that proton-producing redox reactions of oxyanions are expected to be autocatalytic and to manifest propagating acidity fronts. The conditions of proton production in redox reactions are established and verified experimentally by the reactions of $S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_2O_4^{2-}$, SO_3^{2-}, $S_2O_6^{2-}$, and $N_2H_5^+$ with BrO_3^-, IO_3^-, ClO_3^-, ClO_2^-, and $S_2O_8^{2-}$. Twenty new propagating acidity front reactions have been discovered among the possible combinations of these reactions.

Propagating reaction fronts in autocatalytic reactions were discovered by Luther[1] in 1906. His discovery, however, seems to have been forgotten until recently.[2] Interest in the study of propagating acidity fronts and other forms of chemical waves was renewed after the discovery[3] and interpretation[4] of the fascinating Belousov–Zhabotinsky (BZ) reaction.

The number of reaction systems exhibiting chemical-wave behavior, apart from the various modifications of the original BZ system[5-11] is less than 20.[12-21] Three of them, the hydrolysis of alkyl sulfates[1] and the iodate–arsenite[21] and the chlorite–thiosulfate[17,22] systems are characterized by propagating acidity fronts; i.e., the diffusion of the proton produced in the reaction is coupled to its catalytic effect.

The considerations below show that propagating acidity fronts are a generally expected phenomenon in proton-producing redox reactions of oxyions.

Chemical Considerations

It is well-known that the structure of most oxyanions in deprotonated form is symmetrical; the bond order of the central atom–oxygen bonds is higher than 1. Breaking strong bonds in a symmetrical structure requires a high activation energy. Thus the oxyanions are expected to be kinetically stable against redox transformation in alkaline medium. In protonated form, however, the original symmetry is lost, the order of one of the central atom–oxygen bonds decreases to 1. In other words, protonation is expected to decrease the kinetic stability of the oxyanion, making redox transformations more facile.

It follows from these qualitative considerations that proton-producing redox reactions of oxyanions may be expected to be autocatalytic and to manifest a propagating acidity front, if the reactants are mixed in alkaline solution and a drop of acid is used to initiate the reaction in an originally homogeneous unstirred solution.

Proton production is easy to anticipate from the stoichiometry of the reaction. Oxidizing agents usually consume protons and electrons, while reducing agents liberate both species. Therefore,

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if the reducing agent liberates more protons per electron than the oxidizing agent consumes, then the net effect is the acidification of the reaction mixture.

For a more quantitative treatment let us take a general oxyion $A_bO_c^{\,d}$ which is reduced to $A_kO_l^{\,m}$, while another ion, $B_fO_g^{\,h}$ is oxidized to $B_pO_r^{\,s}$. b, c, k, l, f, g, p, and r are the appropriate stoichiometric numbers, d, m, h, and s stand for the charges of the ions. c, l, g, r, d, m, h, and s may be 0. The redox reaction in its most general form is

$$aA_bO_c^{\,d} + eB_fO_g^{\,h} + iH_2O = jA_kO_l^{\,m} + nB_pO_r^{\,s} + tH^+ \quad (1)$$

i.e.

$$a\mathrm{Ox}_1 + e\mathrm{Red}_2 + iH_2O = j\mathrm{Red}_1 + n\mathrm{Ox}_2 + tH^+$$

(If the reaction consumes protons, t and i are negative numbers.)

Taking into account the charge and mass balances, $ab = jk$; $ef = np$; $ad + eh = jm + ns + t$; $ac + eg + i = jl + nr$; and $t = 2i$, the following relation can be derived for the ratio of the number of protons produced (t) and the number of electrons (x) transferred in reaction 1

$$t/x = (1 + (\alpha_r^{\mathrm{B}} - \alpha_o^{\mathrm{B}})/\delta_{\mathrm{B}}) - (1 + (\alpha_r^{\mathrm{A}} - \alpha_o^{\mathrm{A}})/\delta_{\mathrm{A}}) \quad (2)$$

where $\alpha_r^{\mathrm{B}} = h/f$; $\alpha_o^{\mathrm{B}} = s/p$; $\alpha_r^{\mathrm{A}} = m/k$; $\alpha_o^{\mathrm{A}} = d/b$; i.e., the average charge of the ions for one central atom. r and o indices denote the reduced and oxidized forms, respectively. δ_{A} and δ_{B} are the changes of oxidation number for each central atom when the $jA_kO_l^{\,m} \rightarrow aA_bO_c^{\,d}$ and the $nB_pO_r^{\,s} \rightarrow eB_fO_g^{\,h}$ transformations take place, respectively. (δ_{A} and δ_{B} are positive numbers.) The change of the oxidation number may be assigned to the central atom (e.g., $SO_3^{2-} \rightarrow SO_4^{2-}$) or to the oxygen atoms in the case of the peroxo compounds, e.g., $2SO_4^{2-} \rightarrow S_2O_8^{2-}$.

Let us take the oxidation of $S_4O_6^{2-}$ by chlorine dioxide as an example to illustrate the use of eq 2.

$$14ClO_2 + 5S_4O_6^{2-} + 22H_2O = 14Cl^- + 20SO_4^{2-} + 44H^+$$

$$t/x = [1 + ((-2/4) - (-2))/3.5] - [1 + (-1)/5] = 10/7 - 4/5 = 22/35$$

It is easy to see that the first term (10/7) expresses the proton/electron ratio liberated by the reducing agent, while the second term (4/5) expresses the proton/electron ratio consumed by the oxidizing agent. These data may be obtained from the appropriate half-reactions independent of the partner in the redox reaction

$$S_4O_6^{2-} + 10H_2O \rightarrow 4SO_4^{2-} + 14e^- + 20H^+$$

proton/electron liberation ratio = 10/7

$$ClO_2 + 5e^- + 4H^+ \rightarrow Cl^- + 2H_2O$$

proton/electron consumption ratio = 4/5

Their algebraic sum gives the proton/electron liberation factor for the net reaction. It follows from eq 2 that the redox reaction liberates protons, if and only if

$$(\alpha_r^{\mathrm{B}} - \alpha_o^{\mathrm{B}})/\delta_{\mathrm{B}} > (\alpha_r^{\mathrm{A}} - \alpha_o^{\mathrm{A}})/\delta_{\mathrm{A}} \quad (3)$$

Equation 3 indicates that the oxidation of reducing agents for which $\alpha_r^{\mathrm{B}} > \alpha_o^{\mathrm{B}}$, i.e., for which the average charge decreases as a result of oxidation, produces more protons than electrons. All oxyanions of sulfur that contain S–S bond(s) belong to this group when they are oxidized to sulfate.

On the oxidizing agent side, the relation $\alpha_r^{\mathrm{A}} < \alpha_o^{\mathrm{A}}$ is favorable for proton production in the net reaction. All of the oxidizing metal ions belong to this group, but they form hydroxide precipitates in alkaline solution. There are only a few other oxygen-containing oxidizing agents, one of them is ClO_2 in the example above, which fulfill this relation. The peroxo compounds also belong to this group, for example, $S_2O_8^{2-}$ when it is reduced to sulfate.

For all of the oxyhalogen ions (ClO_3^-, BrO_3^-, ClO_2^- etc.) $\alpha_r^{\mathrm{A}} = \alpha_o^{\mathrm{A}}$. Thus, as far as stoichiometry is concerned, propagating acidity fronts are expected in their reactions if the reducing agent fulfills the condition $\alpha_r^{\mathrm{B}} > \alpha_o^{\mathrm{B}}$.

Table I. Half-Reactions of the Oxidizing and Reducing Agents

half-reaction	proton/electron → consumption ← liberation
Oxidizing Agents	
$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	1
$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	1
$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	1
$ClO_2^- + 4H^+ + 4e^- \rightarrow Cl^- + 2H_2O$	1
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	0
Reducing Agents	
$2SO_4^{2-} + 10H^+ + 8e^- \leftarrow S_2O_3^{2-} + 5H_2O$	5/4
$4SO_4^{2-} + 20H^+ + 14e^- \leftarrow S_4O_6^{2-} + 10H_2O$	10/7
$2SO_4^{2-} + 8H^+ + 6e^- \leftarrow S_2O_4^{2-} + 4H_2O$	4/3
$SO_4^{2-} + 2H^+ + 2e^- \leftarrow SO_3^{2-} + H_2O$	1
$2SO_4^{2-} + 4H^+ + 2e^- \leftarrow S_2O_6^{2-} + 2H_2O$	2
$N_2 + 5H^+ + 4e^- \leftarrow N_2H_5^+$	5/4

Table II. Front Characters of the Reactions Studied (Velocity of the Propagating Acidity Front Is Given in 10^3 mm/s)[a]

	$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_2O_4^{2-}$	SO_3^{2-}	$S_2O_6^{2-}$	$N_2H_5^+$
BrO_3^-	C 2.5	C 3.0	C 5.7	F	C 1.3	C 9.7
IO_3^-	N	N	C 510	C 70	C 1.0	C 8.3
ClO_3^-	N	C 0.67	N	N	P 1.0	N
ClO_2^-	C ref 17	C 108	F	F	C 87	F
$S_2O_8^{2-}$	P 1.0	P 1.7	P 2.5	P 1.3	P 1.3	P[b]

[a] C = complete front; P = partial front; F = fast reaction without front; N = no reaction. [b] Observed in a Petri dish.

There is another possibility of acidification of the reaction mixture not directly seen from the stoichiometry. This is the case in which the reducing agent is a much stronger base than its oxidized product. One example is the oxidation of arsenite by iodate,[21] studied and explained by Harrison and Showalter. The same possibility arises in the case of the reducing nitrogen-containing bases, for example, hydrazine or hydroxylamine. Their solution is basic even in partly protonated form, thus they liberate protons when oxidized to nitrogen.

To sum up, there are two types of reducing agents conducive to propagating acidity fronts: (1) all oxyanions of sulfur that contain S–S bond(s); (2) reducing agents that are significantly more basic than their oxidized counterparts, for example, $H_3AsO_3 \rightarrow H_3AsO_4$; $H_2N\text{–}NH_3^+ \rightarrow N_2 + H_2O$, or $SO_3^{2-} \rightarrow SO_4^{2-}$.

As to oxidizing agents, peroxo compounds and oxidizing metal compounds that are stable in alkaline solution (e.g., $[Fe(CN)_6]^{3-}$) are suitable for producing propagating fronts in their redox reactions.

Starting from the above analysis, the oxidizing and reducing agents summarized in Table I have been studied experimentally in all possible combinations in order to see if they manifest propagating acidity fronts in their reactions.

Experimental Section

The highest quality chemicals available have been used to make up slightly alkaline reaction mixtures, containing appropriate acid–base (phenolphthalein, methyl orange, or xylenol orange) indicators. The solution was transferred to a glass tube of internal diameter 2 mm. The wave was initiated at the end of the tube by a drop of 0.1 M H_2SO_4, and its propagation was followed visually in the horizontal direction, except for the reactions of $N_2H_5^+$, where the position was vertical because of the N_2 gas formation.

The reaction of $N_2H_5^+$ with $S_2O_8^{2-}$ was studied in a Petri dish only, because of N_2 formation. In other reactions of $N_2H_5^+$, N_2 formation did not disturb the velocity measurements as the density of the reaction products prevented undesired turbulence. As the aim of our studies was the detection of the wave only, no strict temperature control was applied.

Table III. Concentration of the Reactants in mol dm^{-3}

Ox	Red	$S_2O_3^{2-}$	$S_4O_6^{2-}$	$S_2O_4^{2-}$	$SO_3^{2-} + HSO_3^-$	$S_2O_6^{2-}$	$N_2H_5^- + N_2H_4$
BrO_3^-	Red	0.07	0.015	0.05	0.045 + 0.045	0.05	0.18 + 0.0
	BrO_3^-	0.10	0.04	0.05	0.03	0.02	0.126
	OH^-	0.002	0.01	0.01		0.01	
IO_3^-	Red	0.07	0.017	0.02	0.015 + 0.015	0.05	0.03 + 0.03
	IO_3^-	0.10	0.04	0.02	0.01	0.008	0.02
	OH^-	0.001	0.005	0.02		0.008	
ClO_3^-	Red	0.07	0.025	0.02	0.05 + 0.05	0.05	0.2 + 0.0
	ClO_3^-	0.10	0.20	0.02	0.033	0.05	0.133
	OH^-	0.001	0.004	0.01		0.024	
ClO_2^-	Red	see:	0.005	0.02	0.05 + 0.05	0.05	0.2 + 0.0
	ClO_2^-	Ref. 17	0.020	0.03	0.05	0.02	0.15
	OH^-		0.001	0.05		0.006	
$S_2O_8^{2-}$	Red	0.01	0.01	0.01	0.02 + 0.0	0.04	0.02 + 0.005
	$S_2O_8^{2-}$	0.04	0.07	0.07	0.02	0.04	0.05
	OH^-	0.01	0.004	0.006		0.01	

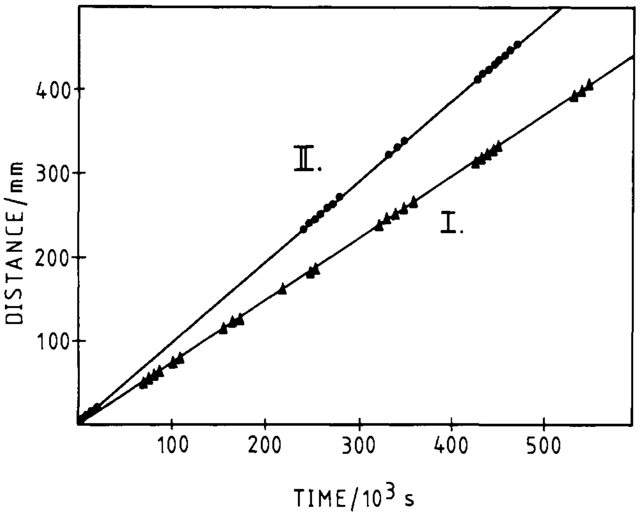

Figure 1. Complete acidity front reactions: (I) [$S_2O_6^{2-}$] = 0.05 M, [BrO_3^-] = 0.02 M, [OH^-] = 0.01 M; (II) [$S_2O_3^{2-}$] = 0.07 M, [BrO_3^-] = 0.1 M, [OH^-] = 0.002 M.

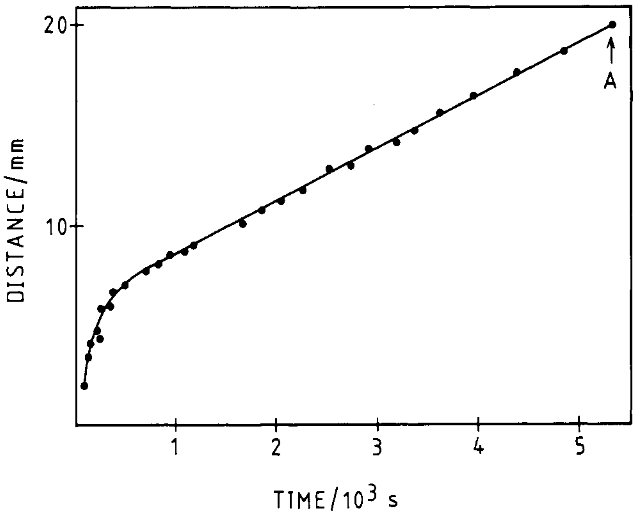

Figure 2. Partial front reaction: [$S_2O_8^{2-}$] = 0.02 M, [SO_3^{2-}] = 0.02 M. A is the last point visually observable.

The measurements were carried out at ambient temperature, 22 ± 2 °C.

Results

The front behavior of the 30 reactions studied and shown in Table II can be classified into the following four groups.

a. Complete Front Reaction (C). In this group of reactions, the propagation of the acidity front is completed before the bulk reaction (which takes place in alkaline solution) uses up the reactants. In this type of reaction, propagation of the front can be observed from one end to the other of a 500–1000 mm capillary. Thirteen of the reactions studied show complete front reaction character.

b. Partial Front Reactions (P). In this group of reactions, propagation of the acidity front can be observed only for a limited time and distance because the bulk reaction is faster than in the previous case. The typical time for which this type of front persists is between 5000 and 30000 s in the seven reactions. One reaction of ClO_3^- and all six reactions of $S_2O_8^{2-}$ show partial front reaction character.

c. Fast Reaction without Front Behavior (F). Reactions in this group are too fast, even in alkaline solution, and therefore they do not exhibit any front character.

d. No Reaction in Either Alkaline or Acidic Solutions (N). The horizontal velocities of the propagating acidity fronts are also included in Table II. The concentrations of the reactants are given in Table III. Examples of complete acidity fronts are shown in Figure 1. The propagation of the front in the cases of $BrO_3^- + S_2O_3^{2-}$ and $BrO_3^- + S_2O_6^{2-}$ is very slow, but it could be followed for up to 4–6 days!

Partial acidity fronts are shown in Figure 2. The characteristic behavior of this type of front is that after an initial, fast propagation of the front, a slower constant speed is established, the observation of which is stopped by the disappearance of the indicator color, because of the bulk reaction. Propagation data collected in Table I were calculated from the lower constant speed. The faster initial velocity evidently results from the diffusion of protons from the 0.1 M H_2SO_4 needed to initiate the reaction.

For the sake of completeness we have attempted to produce acidity fronts with $[Fe(CN)_6]^{3-}$ as oxidizing agent. No wave behavior could be detected in these reactions, probably because the proton concentration has no significant effect on the simple $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$ electron transfer.

Conclusion

It is evident that a propagating acidity front is expected if the reaction that produces protons is relatively slow in alkaline and fast in acidic solution. The considerations and the results presented prove convincingly that propagating acidity fronts are not curiosities, but rather they are fairly general characteristics of proton producing inorganic redox reactions. Taking into account that the reduced forms of the oxyanions are generally more basic than their oxidized counterparts ($AsO_3^{3-} \rightarrow AsO_4^{3-}$, $SO_3^{2-} \rightarrow SO_4^{2-}$, $H_2PO_3^- \rightarrow H_2PO_4^-$, etc.), the detection of many more propagating acidity fronts can be expected in the near future.

The acidity fronts in the reactions studied have been artifically generated by a drop of acid. It is evident, however, that if a local acidification takes place anywhere in the solution, it can generate a chemical wave and transfer the system into its thermodynamically stable state.

Our future efforts will be concentrated to reveal the circumstances in which local acidification due to fluctuations may take place. Our ultimate aim is to find and interpret more systems exhibiting the theoretically predicted[23] and recently experimentally verified[22,24,25] fluctuation-induced reactions.

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Registry No. $S_2O_3^{2-}$, 14383-50-7; $S_4O_6^{2-}$, 15536-54-6; $S_2O_4^{2-}$, 14844-07-6; SO_3^{2-}, 14265-45-3; $S_2O_6^{2-}$, 14781-81-8; $N_2H_5^+$, 18500-32-8; BrO_3^-, 15541-45-4; IO_3^-, 15454-31-6; ClO_3^-, 14866-68-3; ClO_2^-, 14998-27-7; $S_2O_8^{2-}$, 15092-81-6.

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Molecular Structures of Unstable Dichloroketene and Its Precursor, Trichloroacetyl Chloride, from Electron Diffraction[1]

B. Rozsondai,[2a] J. Tremmel,[2a] I. Hargittai,*[,2a] V. N. Khabashesku,[2b] N. D. Kagramanov,[2b] and O. M. Nefedov[2b]

Contribution from the Structural Chemistry Research Group of the Hungarian Academy of Sciences, Eötvös University, Budapest, Pf.117, H-1431, Hungary, and the Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913, USSR. *Received August 1, 1988*

Abstract: The molecular structure of dichloroketene, Cl_2CCO, has been determined at room temperature by electron diffraction. Cl_2CCO was produced from trichloroacetyl chloride, Cl_3CCOCl, with zinc at 420 °C during the diffraction experiment. Analysis of data of the reaction product, containing about 30% of trichloroacetyl chloride, has yielded the following geometrical parameters (r_a) of Cl_2CCO, with estimated total errors: C=C 1.299 ± 0.005, O=C 1.160 ± 0.003, Cl—C 1.726 ± 0.004 Å, and ∠Cl—C=C 120.4 ± 0.2°. The structure of Cl_3CCOCl has been determined separately from diffraction data of its vapor. For a model in which the O=C bond eclipses a Cl—CCl_2 bond, the bond lengths (r_a) and angles are C—C 1.540 ± 0.008, O=C 1.191 ± 0.004, Cl—CO 1.727 ± 0.017, Cl—CCl_2 1.774 ± 0.006 Å, ∠C—C=O 121.4 ± 0.7°, ∠C—CO—Cl 113.8 ± 0.7°, $\angle(\text{Cl—C—CO})_{\text{mean}}$ 109.7 ± 0.4°.

I. Introduction

The geometric and electronic structures of highly reactive ketene derivatives have motivated several recent studies on monohalogeno- and dihalogenoketenes by microwave,[3,4] infrared[5-7] and photoelectron spectroscopy,[8,9] and ab initio calculations.[4] Geometrical parameters were obtained for ClHCCO from microwave spectra,[3] and for FHCCO from ab initio calculations.[4] Dichloroketene, Cl_2CCO, was shown to have a very small dipole moment, and its microwave spectrum could not be observed.[6]

In the present work we have undertaken the structure determination of dichloroketene. This is a continuation of our studies of unstable species that have so far included halogenated carbene analogues AX_2 (A = Si, Ge; X = Cl, Br[10]) and the allyl radical.[11]

Cl_2CCO was generated from trichloroacetyl chloride, Cl_3CCOCl, in a flow system during the diffraction experiment, and the reaction product was a mixture of the two substances. Although the structures of other halogen-substituted acetyl halides have been published,[12-15] no structure determination of Cl_3CCOCl is known to us. Thus, the study of Cl_2CCO had to be accompanied by the structure analysis of Cl_3CCOCl.

II. Experimental Section

Trichloroacetyl chloride was obtained from Cl_3CCOOH by its reaction with $SOCl_2$ and purified by distillation and repeated vacuum freezing.[7] Dichloroketene was produced by the high-temperature reaction of vapors of Cl_3CCOCl with metallic zinc:[8]

$$Cl_3CCOCl + Zn \xrightarrow{\Delta} Cl_2CCO + ZnCl_2$$

Figure 1 shows the schematic arrangement of the reactor nozzle system. The quartz tube (4) of 7-mm inner diameter tapers in a nozzle (11) of 0.4-mm outlet diameter. This end of the tube is covered with a graphite layer and is contacted to an earthed metal block (10) to prevent charging by the electron beam. The heated zone (7a), which is 7 cm long, lies outside the diffraction chamber, at about 30-cm distance from the nozzle. The construction of the connection and the sealing between the tube and the wall of the chamber ensured a stable position of the nozzle regardless of temperature changes in the reaction zone. Our previous experience[7] and investigations of vapor composition by a quadrupole mass spectrom-

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(1) This paper is dedicated to the memory of Andrei K. Maltsev (1933–1986), one of the pioneers of structural research of unstable species.

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