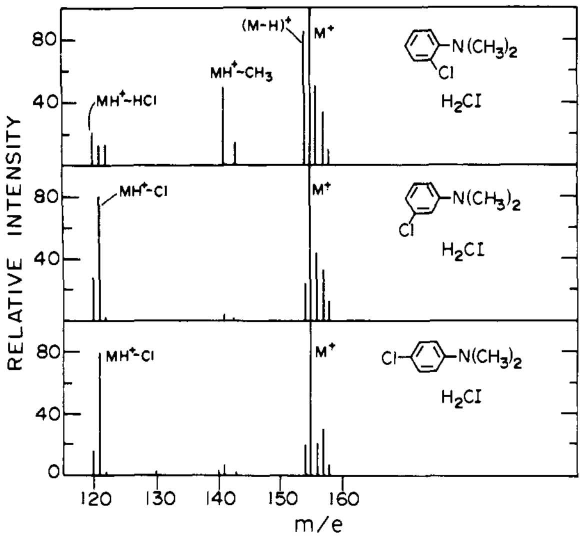

Figure 5. H_2 Cl mass spectra of isomeric *N,N*-dimethylchloroanilines.

H]$^+$, which may arise either by H_2 loss from MH^+ or by direct hydride obstruction by $H_3^{+}\cdot$, and to the odd-electron $ClC_6H_4NHCH_3^{+}\cdot$ ion, arising by methyl radical loss from MH^+. The loss of the chlorine substituent is of only minor importance with loss of HCl from MH^+ being more prominent than loss of Cl· from MH^+. For the meta and para isomers the formation of both $[M - H]^+$ and $MH^+ - CH_3$ is of greatly reduced importance, the major fragment ion observed corresponding to the odd-electron *N,N*-dimethylaniline molecular ion arising by loss of Cl· from the protonated molecule. Thus, for this system as well, the major fragmentation reactions of the protonated molecule involve formation of odd-electron products. The enhanced formation of the $MH^+ - CH_3$ product by the ortho substituent also is observed for the haloanisoles where the $MH^+ - CH_3$ product is much more significant for the ortho isomer than for the meta and para isomer. This rather strong ortho effect can be rationalized if one assumes that for the ortho-substituted compound protonation occurs at the substituents to give, effectively, a disolvated proton. Loss of CH_3 from this species can readily yield the respective halophenol or haloaniline odd-electron molecular ion. Such disolvation cannot occur when the substituent is meta or para and formation of $MH^+ - CH_3$ is greatly reduced.

Acknowledgment. The authors are indebted to the National Research Council of Canada for financial support and to Professor F. W. McLafferty for communication of results (ref 13) prior to publication.

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(15) Because of the numerous sequential reactions with H_2 (Scheme I) the spectra of dichloro- and difluorobenzene are strongly dependent on the reagent gas pressures and ion-source residence time. For example, the spectrum for $Cl_2C_6H_4$ in Figure 4 was recorded at a lower H_2 pressure than the spectrum reported previously[3] where $C_6H_7^+$ was observed as the base peak.

ESR Evidence for a Biradical Dimer Initiator in Diacetylene Polymerization

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Abstract: Single-crystal monomers of 5,7-dodecadiyne-1,12-diol bis(phenylurethane) X-ray irradiated at 77 K give rise to an ESR spectrum at 77 K consisting primarily of lines due to radical pairs along with some weaker lines due to $S = 1/2$ radicals. The radical pair is a biradical of a diacetylene dimer with D = 732 G and E = 26.5 G and appears to be the initiator of solid-state polymerization of X-ray irradiated TCDU crystals at low conversion.

Introduction

Single crystals of disubstituted diacetylene monomers are capable of producing highly perfect crystals of conjugated polymers by solid-state polymerization.[1-5] Initiation may be by heat, light, or high-energy radiation. The 1,4-addition polymerization of diacetylene single crystals leads to two possible mesomeric structures, I and II. Examples of structures I[6] and II[7,8] have been studied by X-ray diffraction and Raman spectroscopy.

$$\underset{\text{I}}{-(R)C{=}C{=}C{=}C(R)-} \qquad \underset{\text{II}}{=(R)C{-}C{\equiv}C{-}C(R){=}}$$

The solid-state polymerization mechanism of diacetylene single crystals has become of considerable interest in the past

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few years. For instance, there appear to be two possible processes for polymerization, a radical mechanism and a carbene mechanism, involving radicals III and IV, respectively. Chance and his co-workers[9-11] suggested the radical mechanism based on thermodynamic and kinetic arguments. On the other hand, Wegner and his co-workers[12-14] showed evidence for the carbene process based on spectroscopic measurements.

$$\text{(oligomer)—(R)C=C=C=C—R}$$

III

$$\text{(oligomer)=(R)C—C}\equiv\text{C—}\ddot{\text{C}}\text{—R}$$

IV

Recently, ESR studies were extensively carried out during thermal polymerization at high temperature by Stevens and Bloor[15,16] and others[17,18] and UV irradiation at 4 K by Bubeck et al.[19] for poly[1,2-bis(*p*-tolylsulfonyloxymethylene)-1-buten-3-inylene], generally referred to as PTS. The PTS polymer structure is the mesomeric structure (II). In fully polymerized PTS single crystals, a single Lorentzian ESR line centered at $g = 2.0023$ is observed.[15,17] This spectrum is assigned to a mobile defect or a bond alternation defect in which the position of the defect may fluctuate. During the polymerization of PTS, triplet ESR signals[16-19] were observed and assigned to the carbene IV thought to be the active species of polymerization.

On the other hand, when we X-irradiated PTS monomer single crystals[20] at 77 K, to a low dose of only 0.5 Mrad, $S = \frac{1}{2}$ species were mainly produced with a small amount of carbene. This $S = \frac{1}{2}$ radical was assigned as radical III. In addition to this observation, radical III changed to polymer I and then to polymer II when an X-irradiated monomer single crystal of PTS was gradually warmed. We thus concluded[20] that the radical mechanism is operative at low radiation dosage in the X-ray initiated solid-state polymerization of diacetylene single crystals.

In this paper, we report the ESR spectrum and structure of radical pairs (biradicals) which are produced when a 5,7-dodecadiyne-1,12-diol bis(phenylurethane) (referred to as TCDU) monomer single crystal is X-irradiated to a dose of 1 Mrad at 77 K. Structurally, TCDU is the diacetylene $\text{R—C}\equiv\text{C—C}\equiv\text{C—R}$ where $\text{R} = \text{-(CH}_2)_4\text{OCONHPh}$. Evidence will also be presented to suggest that this biradical is an initiator of the polymerization process in diacetylene compounds in agreement with a previous mechanism proposed by Chance and co-workers.[10]

Experimental Section

Single crystals of the TCDU monomer were kindly supplied by A. F. Preziosi of Allied Chemical Corp. The TCDU monomer crystals were mounted on Suprasil rods and X-ray irradiated at 77 K to a dose of about 1 Mrad. To record the temperature dependence of the ESR spectra, we employed a different approach than previously reported to avoid the ESR signal from the color centers of irradiated quartz. A crystal was irradiated at 77 K in a sample holder made from polystyrene foam and transferred into another sample holder at 77 K without warming. ESR measurements were made at 77 K.

The TCDU polymer crystals belong to the monoclinic space group $P2_1/a$ with $a = 6.229$ Å, $b = 39.027$ Å, $c = 4.909$ Å, and $\beta = 106.85°$. Each unit cell contains two polymer chains with the axis of the polymer chain lying parallel to the *c* axis.

The ESR spectra were recorded with a Varian E-12 X-band spectrometer. The magnetic field was measured with a tracking NMR gaussmeter and the klystron frequency was measured by a Hewlett-Packard frequency counter, Model 5246L. The ESR spectra were recorded at 10° intervals in the *a*b*, *bc*, and *ca** planes at 77 K by detecting the second harmonic of 50-kHz field modulation.

Here we assumed the monoclinic, *a**, *b*, and *c* axis directions of the TCDU polymer to be those of the TCDU monomer crystal since the crystal structure of the TCDU monomer has not been determined This assumption seems to be reasonable since the macromorphology of the TCDU crystal does not change during polymerization.

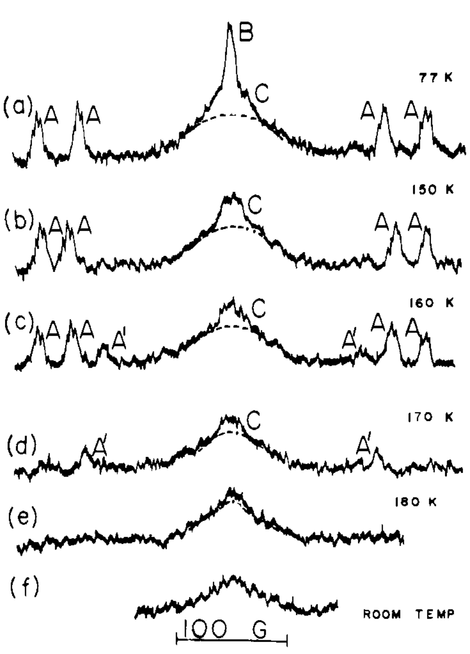


Figure 1. The second-derivative ESR spectra of a single crystal monomer of TCDU X-irradiated at 77 K and observed at (a) 77 K and after annealing for 15 min at (b) 150 K, (c) 160 K, (d) 170 K, (e) 180 K, and (f) room temperature. The magnetic field is nearly parallel to the *c* axis except in (d) where $H \| c$. All ESR spectra shown were recorded at 77 K.

The ESR spectrum was followed as a function of temperature between 77 K and room temperature in addition to visually observing the color change of the TCDU monomer crystal. To avoid any errors in measuring ESR spectral intensities due to differences in microwave power saturation, all spectra were recorded at 77 K after the crystal had been annealed at higher temperatures.

Results

The second-derivative ESR spectrum of the X-irradiated TCDU monomer crystal observed at 77 K without warming is shown in Figure 1. After the irradiated crystal has been annealed for 15 min at 150, 160, 170, and 180 K and room temperature, the ESR spectrum obtained upon recooling to 77 K following each annealing is given in Figures 1b, 1c, 1d, 1e, and 1f, respectively.

The spectrum at 77 K without warming consists of four A peaks, a B peak, a C peak, and an impurity signal. The impurity signal arises from the sample holder and is indicated by the broken line shown in Figure 1. The B peak decays completely after annealing at 150 K. Since the *g* value of this peak is 2.0023 ± 0.0002, we have temporarily assigned it as due to a trapped electron. The C peak remains until the sample is warmed to 180 K. Analysis shows that the C peak exhibits the features of an $S = \frac{1}{2}$ radical; however, owing to the weak radical intensity and poor resolution, we did not attempt a complete study of radical C. An important point to note is the ratio of intensities between the A and C peaks. The intensity of the A peak is considerably greater than that of the C peak if the impurity peak underlying C is removed. This means that the concentration of the radical which gives rise to the A lines is greater than that due to the C peak. At 160 K, the A peaks began to decay and new A′ peaks appear. However, as the temperature is raised to 180 K, the A′ peaks have also completely disappeared. A complete angular dependence of the separation between the high- and low-field A line is given in Figures 2, 3, and 4 when the crystal is rotated about the (0,0,1), (cos 4°,0,sin 4°), and (0,1,0) directions, respectively. The angular dependence in Figures 3 and 4 shows that the separation crosses through zero, giving rise to a positive and neg-

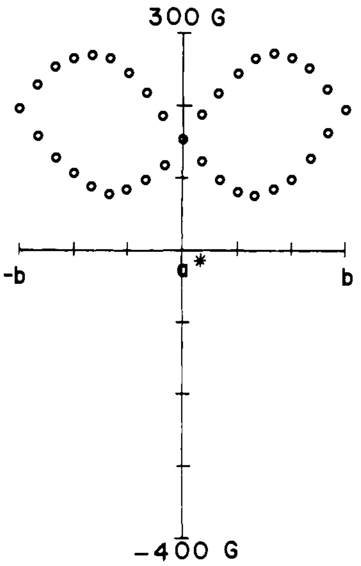


Figure 2. The angular dependence of the peak-to-peak separation of the high- and low-field A lines while rotating about the (0,0,1) direction.

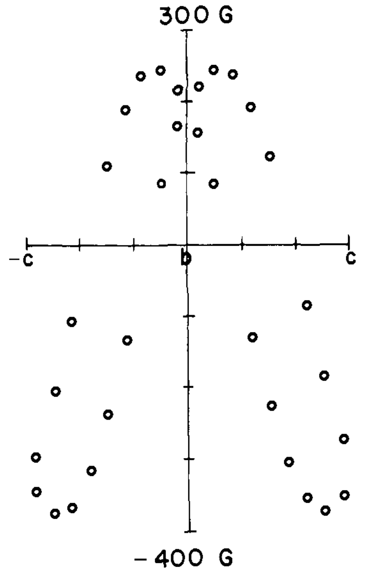


Figure 3. The angular variation of the peak-to-peak separation of the high- and low-field A lines while rotating about the (cos 4°,0,sin 4°) direction.

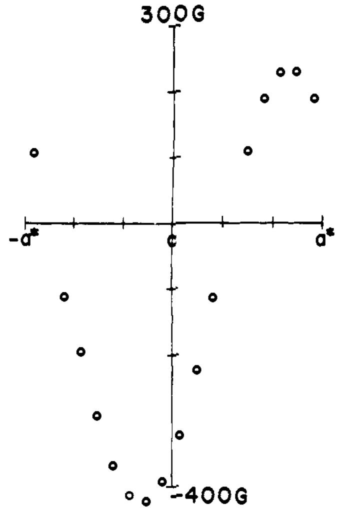


Figure 4. The angular variation of the peak-to-peak separation of the high- and low-field A lines while rotating about the (0,1,0) direction.

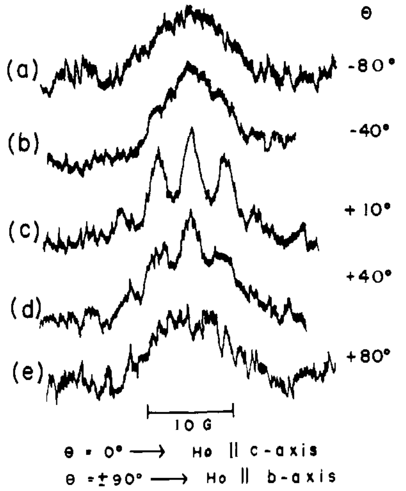


Figure 5. The angular variation of the superhyperfine coupling in the *bc* plane which splits each A line at 77 K.

ative separation, although the sign is arbitrary. Such features arise for radical pairs and not for $S = 1/2$ radicals and thus the A lines have been assigned to radical pairs. A complete study of the angular dependence of the A′ lines was not tried because of the low intensities. However, enough data was acquired to show that the A′ lines are also due to radical pairs.

It was also observed that, when the irradiated crystals were warmed from 160 to 180 K, not only did radical lines A and A′ disappear but the color of the X-irradiated TCDU monomer crystal changed from colorless to bright red. Upon recooling the crystal to 77 K, lines A and A′ did not reappear and the red color remained. This irreversible color change was taken as evidence that the polymerization of the TCDU monomers occurred between 160 and 180 K. No other ESR signals were observed over this temperature range.

The angular dependence of the hyperfine couplings which appear to split each A line is shown in Figure 5 for the $\Delta M_s = 1$ transition in the *bc* plane. When $\theta = 10°$, the separation between adjacent lines is 3.75 G, which means hyperfine couplings equal to 7.5 G. From the intensity pattern the couplings may be due to four nearly equivalent protons or to two equivalent protons and one nitrogen with $A_N = A_H$.

To determine the zero-field couplings D and E for radical pair A, we neglect the hyperfine couplings and make use of the Hamiltonian[21]

$$\mathcal{H} = \beta H_0(\mathbf{S}_1 + \mathbf{S}_2)\cdot\mathbf{g}\cdot\mathbf{h} + \mathbf{S}_1\cdot\mathbf{D}'\cdot\mathbf{S}_2 \tag{1}$$

$$\mathbf{D}' = (g\beta)^2 \left\|\left(\frac{\mathbf{E}}{r^3} - 3\,\frac{\mathbf{r}\cdot\mathbf{r}}{r^5}\right)\right\| \tag{2}$$

where g is the average g value, r is the vector between spin 1 and spin 2, and **h** is the direction cosine of the applied external magnetic field.

From these equations, the distance (d) between $\Delta M_s = \pm 1$ transitions can be expressed as[21]

$$d = 3(\tilde{\mathbf{h}}\cdot\mathbf{D}'/2\cdot\mathbf{h})/g\beta$$

$$d = \tilde{\mathbf{h}}\cdot\mathbf{D}\cdot\mathbf{h} \tag{3}$$

$$\mathbf{D} = \frac{3g\beta}{2r^3}\left\|\left(\mathbf{E} - \frac{3\mathbf{r}\cdot\tilde{\mathbf{r}}}{r^2}\right)\right\| \tag{4}$$

An undiagonalized tensor **D** was deduced from the angular variation in Figures 2–4, and upon diagonalization resulted in two sets of principal values and direction cosines. The correct set of values was determined by measuring the angular variation of the A lines in a fourth plane that was positioned skew to *a*b*, *bc*, and *ca** planes. These values are given in Table I.

An additional experiment was also carried out in which a single crystal of the TCDU polymer was X-irradiated at 77 K to a dose of 1 Mrad and studied by ESR at 77 K. No measurable concentration of radical pairs nor any significant amounts of a $S = 1/2$ radical were observed. The polymer crystal was produced by exposing a monomer crystal of TCDU to 50 Mrad of γ-irradiation at room temperature. At this dosage 80-90% of the polymer is polymerized. Upon further irradiation at 77 K, no ESR lines are expected to be observable from the 10-20% of the remaining monomer as the ESR spectral intensity observed for the irradiated pure monomer is already quite weak (Figure 1).

Discussion

The electron density distribution can be estimated for the radical pair A from the magnitude of the D and E terms given in Table I. However, because the E term is nonzero, it is obvious that a point-dipole approximation such as eq 5 is not a proper description of the radical-radical interaction.

$$d = \left(\frac{3}{2}\right) g\beta/r^3(1 - 3\cos^2\theta) \qquad (5)$$

θ is the angle between the spin-spin direction and the external magnetic field. An alternative approximation would be to assume that a half point-charge is located in each of the two lobes of each p_π orbital and that the two half point-charges are separated by 1.4 Å.[22] This also assumes that each spin is localized on one atom. However, even with such an approximation, we cannot reproduce such a large E (26.5 G) value when D = 732 G. From these considerations, we conclude that the spin is delocalized among several atoms on each half of the radical pair.

From the observation of superhyperfine coupling structure in the *bc* plane, the molecular structure of each radical in the radical pair can be deduced. The TCDU monomer structure will be numbered in the following manner: $R—C^1{\equiv}C^2—C^3{\equiv}C^4—R$ where $R = \text{-}C^5H_2C^6H_2C^7H_2C^8H_2OC^9ONHPh$. From the previous section, the experimental results can be summarized as follows.

(1) Radical pair A is an initiator of solid-state polymerization of diacetylene compounds.

(2) The amount of radical pairs is larger than that of $S = 1/2$ species when the TCDU-monomer crystal is X-irradiated at 77 K.

(3) There are no radical pairs when a polymer crystal of TCDU is X-irradiated under the same conditions as that used for the monomer.

(4) The spin-spin direction of radical pair A is close to the polymer chain direction (refer to D_{zz} direction in Table I).

(5) The spin distribution in each half of the radical pair is delocalized.

(6) Each half of the radical pair has hyperfine couplings less than 7.5 G and may have at least two equivalent protons.

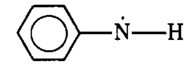
There are two different possibilities for the parent radical; one is a main-chain radical and the other is a side-group radical. Observations (1), (2), and (3) strongly suggest that the parent radical is a main-chain radical. For instance, if a side-group radical is formed, it would be difficult to rationalize (a) that the side-group radical causes polymerization and (b) that the radical pair is selectively created by X-irradiation.

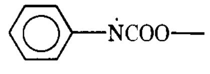
In addition to the implications of results (1), (2), and (3), we can also examine the structure of the five possible radicals that can be produced in irradiated TCDU monomers. They are (1) the carbon-centered radical in which spin is localized on C^5–C^8 V, (2) VI, (3) VII, (4) VIII, and (5) IX. We can easily eliminate radical V by observations (5) and (6) because radical V should have localized spin and large hyperfine couplings. Also nitrogen-centered radicals VI and VII can be excluded since experimentally four nearly equivalent protons or two equivalent protons and one nitrogen with $A_N = A_H$ are observed. Thus there is no possibility that both of the parent radicals of the radical pair are VI or VII.[23] An alternative possibility is that one of them is VI or VII and the other is a radical which is VIII, IX, or a main-chain radical. The combination between VI or VII and a main-chain radical is impossible because of the D_{zz} direction. The possibility of VIII or IX can be excluded by arguments given below.

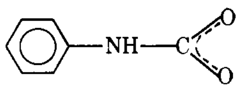
Table I. Principal Values of the **D** Tensor, Direction Cosines, and Related Parameters for the Biradical A

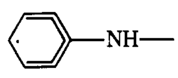
		direction cosines[a]		
	G	⟨*a**⟩	⟨*b*⟩	⟨*c*⟩
D_{zz}	−488	−0.3385	∓0.2956	0.8933
D_{yy}	270	−0.5212	±0.8494	0.0835
D_{xx}	217	0.7834	±0.4373	0.4416
$\lvert D\rvert$	732			
$\lvert E\rvert$	26.5			
r_{eff}[b]	4.85 Å			

[a] The *a**, *b*, *c* directions of the polymer were experimentally determined by the Laue method. [b] $|D| = \frac{3}{2}(3g\beta/r_{\text{eff}}^3)$.

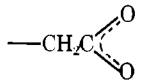

VI


VII


VIII

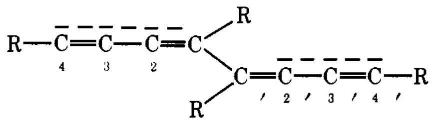

IX

Radicals analogous to VIII are ones of the type[24] i. Such radicals exhibit no discernible proton hyperfine couplings and possess large g anisotropy. This is not observed in the present study. Thus radical VIII must be deleted as a possibility. The possibility of a phenyl radical (IX) is next considered because of observations (4), (5), and (6).

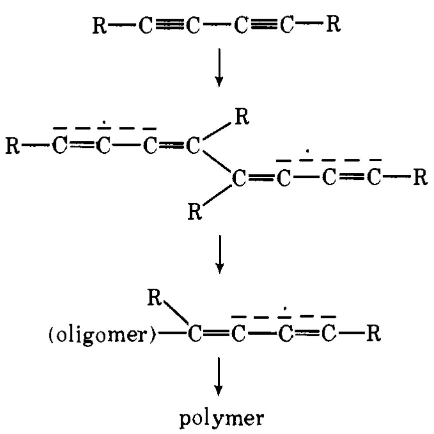

i

Recently, the radical pairs in benzene were observed by Matsuyama and Yamaoka.[25] They used a dose of 1000 Mrad γ-irradiation compared to our 1-Mrad dose of X-irradiation. They observed radical pairs involving the phenyl and benzyl radicals with the radical-pair intensity about 100 times less than that of $S = 1/2$ species. In contrast, we did not observe benzyl radicals and also noted that the ratio of the radical pairs intensity to the $S = 1/2$ species was greater than one. These facts indicate that our radical pair is not the phenyl radical pair.

From the above arguments, we conclude that the radical pair as an initiator of polymerization in TCDU monomer crystals is the main-chain biradical (X). This assignment is supported by the fact that the spin-spin direction is close to the polymer chain and that r_{eff} = 4.85 Å, the intrachain distance. It is also possible for biradical X to be the initiator of polymerization


X

Scheme I



27° of biradical X must occur before polymerization is complete. In comparison, the proton couplings found for the $S = \frac{1}{2}$ intermediate in PTS[20] are larger (7.5 vs. 16 G), indicating that either the spin density on C^4 is smaller for X than that for the intermediate in PTS or a difference occurs in the orientation of the side group. Furthermore, it may be possible that the other radical pair observed (peak A′ in Figure 1) may have a different spin distribution and a different configuration than biradical X, and may be the much more favored biradical for polymerization.

In conclusion we have observed that biradical X is an initiator in the solid-state polymerization of TCDU crystal. Combining the results of this study with those found previously for PTS,[20] it is suggested that polymerization proceeds according to Scheme I. From these studies it appear that the solid-state polymerization of diacetylene compounds at low X-ray dosage proceeds principally according to a radical mechanism rather than a carbene mechanism. A radical mechanism is also in good agreement with the findings of Chance and co-workers.[10]

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A Heterogeneous Chemical Oscillator. The Belousov-Zhabotinskii-Type Reaction of Oxalic Acid

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Abstract: A new type of oscillating reaction, the heterogeneous Belousov-Zhabotinskii reaction of oxalic acid, is described. Periodic CO_2 and Br_2 evolution was measured with the aid of flame ionization and coulometric detectors. The stoichiometry of the reaction was determined and a radical mechanism was proposed based on experiments with acrylamide as a radical scavenger. A possible connection with the mechanism of the original Belousov reaction is mentioned.

Introduction

The so-called Belousov-Zhabotinskii (BZ) reaction, the cerium ion catalyzed oscillatory oxidation of several organic compounds by bromate in aqueous sulfuric acid media, is the most studied chemical oscillator.[1-10]

Field, Körös, and Noyes (FKN) developed a detailed theory for the phenomenon especially when the organic component is malonic acid.[1] The essential features of their mechanism are summarized in steps FKN1-FKN5.[2]

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr \quad (FKN1)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr \quad (FKN2)$$

$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O \quad (FKN3a)$$

$$Ce^{3+} + BrO_2\cdot + H^+ \rightarrow Ce^{4+} + HBrO_2 \quad (FKN3b)$$

$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+ \quad (FKN4)$$

$$HOBr + \text{organic matter} \rightarrow \text{bromoorganic compounds} \quad (FKN5a)$$