3. The interaction of 1-trifluoromethylvinylthiobenzoate with NH₃ leads to the cyclic dimers of trifluoroacetone: 2,4-bis(trifluoromethyl)-2-methyl-1,3- and 3,5-bis(trifluoromethyl)-3-methyl-1,2-dithiolane.

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REACTION OF 10-VINYLPHENOTHIAZINE WITH BENZOYL PEROXIDE

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The decomposition of benzoyl peroxide (I) by aliphatic and aromatic amines has been the subject of numerous studies [1], whereas the reaction of nitrogenous heterocyclic monomers with (I) has been investigated only in connection with the mechanism of the initiation of the polymerization of 9-vinylcarbazole [2]. We here show that in the case of another highly reactive electron-donor monomer [3] (10-vinylphenothiazine), the reaction of (I) with (II) may follow several pathways:

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 $\mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} + (\mathbf{PhCOO})_{2} \rightleftharpoons \pi \rightleftharpoons [\mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2}^{\ddagger} (\mathbf{PhCOO})_{2}^{\ddagger}] \rightarrow [\mathbf{R}^{+}, \mathbf{CH} = \mathbf{CH}_{2}, \mathbf{PhCOO}^{-}, \mathbf{PhCOO}^{-}].$ $\mathbf{RH} \xleftarrow{\operatorname{Protic}}_{\text{solvent}} \mathbf{R}^{-} \xleftarrow{\operatorname{Aprotic}}_{\text{solvent}} \xleftarrow{\mathbf{R}^{-}} \mathbf{R} - \mathbf{R}$ $\mathbf{PhCOOH} \xleftarrow{\operatorname{H+}} \mathbf{PhCOO}^{-} \xleftarrow{\mathbf{CH} = \mathbf{CH}_{2}} \mathbf{PhCOO}^{-} \mathbf{R} - \mathbf{OOCPh}$ $\mathbf{PhCOOH} \xleftarrow{\mathbf{H+}} \mathbf{PhCOO}^{-} \xleftarrow{\mathbf{CH} = \mathbf{CH}_{2}} \mathbf{PhCOO}^{-} \mathbf{CH} = \mathbf{CH}_{2}$ $\begin{bmatrix} \mathbf{R} \\ -\mathbf{CH} - \mathbf{CH}_{2} - \mathbf{I}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xrightarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xrightarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xrightarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xrightarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xrightarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{CH}_{2} = \mathbf{CH}} \mathbf{R} - \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{CH}_{2} - \mathbf{CH}_{2} - \mathbf{CH}_{2} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{2} \xleftarrow{\mathbf{PhCOO}^{-}} \mathbf{PhCOO} \begin{bmatrix} \mathbf{R} \\ -\mathbf{R} \\ -\mathbf{R} \end{bmatrix}_{n} \mathbf{CH} = \mathbf{CH}_{n} \mathbf{CH}$

The principal end-products obtained from the reaction of equimolar amounts of (I) and (II) were: unsubstituted phenothiazine, 3,10-biphenothiazine, 3-benzoylphenothiazine, benzoic acid, and poly-(10-vinyl-phenothiazine) containing benzoate groups in the chain. Vinyl benzo-

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Fig. 1. Plots of the energy of the charge-transfer bands of complexes (II) against the half-wave electrochemical reduction potentials and electron affinity energies of acceptors: 1) 7,7,8,8tetracyanoquinodimethane; 2) p-fluoranil; 3) benzoyl peroxide; 4) 1,2-napthoquinone; 5) p-toluquinone; 6) 1,10-anthraquinone; 7) 1,2,3,4-tetrahydrofluorenone; 8) 2,4,5,7-tetranitrofluorenone. [(I)] = 0.02, [(II)] = 0.1 mole/liter.

Fig. 2. Logarithmic plots of the initial rate of formation of the phenothiazine radical against concentration of (I) and (II): 1, 3) in DMF; 2, 4) in toluene.



ate and 1,3-cyclohexadiene were identified amongst the liquid products. Intermediate reaction products included a donor-acceptor (DA) complex, the cation-radical of (II), and its breakdown products, the neutral phenothiazine radical and the vinyl cation.

The first step in this reaction is the formation of the DA complex. This is shown by the appearance of a broad, short-lived absorption band in the region of 560 (λ_{CTB}) in the UV spectra of cooled mixtures (5°C) of (I) and (II). The energy of the observed electronic transition is in close accordance with the overall linear dependence of the energy of the charge-transfer bands (CTB) of the complexes (II) on the electron affinity energies (E_A) and electrochemical reduction potentials (E¹/₂) of other electron acceptors (Fig. 1). The value of E_A for (I) calculated from these plots was 2.2 ± 0.1 eV. The abundance of final and intermediate reaction products of (II) with (I), in contrast to its reactions with other electron acceptors with similar E_A and E¹/₂ values [4], is due to the rapid destruction of the ion-radical components of the DA complex.

It has been found that in the absence of rapid thermolysis and photolysis, (I) decomposes actively on addition of the electron donor (II). Thus, the half-life of (I) in the presence of equimolar amounts (10^{-3} mole) of (II) at 20°C is 1.5 h, whereas the concentration of (I) in pure THF remains unchanged for 20 h. The mechanism of the decomposition of the anion-radical from (I) in the presence of electron-donor amines to give benzoate anions and radicals has been studied thoroughly [1]. We have observed that cation-radicals of (II) decompose in



Fig. 3. Plots of initial rate of formation of phenothiazine radical versus temperature: 1) in toluene; 2) in DMF.

a similar way. The formation of these unstable species in the reaction medium (acetonitrile, 20°C) could only be observed by the use of nanosecond flash photolysis (λ 515 nm [5]). This low stability is due to the rapid destruction of the counterion, i.e., the anion-radical of (I), and to the structural features of (II) which inhibit charge equalization and electron delocalization through the molecule. The kinetics of decomposition of the cation-radicals of (II) were examined with respect to temperature and reagent concentration, using UV spectroscopy to measure the formation of the neutral phenothiazine radical (λ_{max} 380 nm [6]). The kinetic orders of the reactions were calculated from the logarithmic plots of the initial rates of formation of these species against the concentrations of (I) and (II) (Fig. 2). Reaction in nonpolar and polar basic media is characterized by low values for the activation energies, $E_a = 5.8 \pm 0.3$ and 10.9 ± 0.3 kcal/mole, and is described by the following rate equations: $V = k[(II)] \cdot [(I)]^{0.5}$ and $V = k[(II)] \cdot [(I)]^{0.87}$ in toluene and DMF, respectively. The higher value of E_a in DMF shows that there is partial stabilization of the solvate-separated cation-radicals of (II), and confirms the earlier suggestion that destruction of the products of one-electron reduction of (II) by organic electron acceptors takes place within the solvent cell [7].

The reaction then proceeds via radical recombination and neutralization of the ionic species, and the initiation of the polymerization of (II). The product ratios from the reaction of (I) with (II) is dependent on the polarity of the medium, temperature, and reactant concentrations. In polar, protic solvents (methanol), in the presence of catalytic amounts of (I) $(10^{-2}-10^{-3} \text{ mole})$, the principal reaction product is phenothiazine. Furthermore, the reaction mixture was found to contain MeOCH=CH $_2$ and benzoic acid. In aprotic polar and in nonpolar solvents, equimolar amounts of (I) and $(\bar{I}I)$ give 3,10-biphenothiazine,-3benzoylphenothiazine, and $PhCO_2CH=CH_2$. The latter is the product of the neutralization of the benzoate anion by the vinyl cation formed in the decomposition of the cation radical of (II). Polymerization of (II) in the presence of (I) at elevated temperatures is not predominant. The yield of poly(10-vinylphenothiazine) in solvents of low polarity and basicity at 80°C does not exceed 10-13%. The bulk of the products consists of a low-molecular-weight benzoate-containing oligomer (M_n 1600-2800), formed by the fission of the growing macro chains by benzoate radicals and anions. Fission of the polymer chain could also occur by cyclization of the trimer followed by elimination of the phenothiazine substituent to give 1,3-cyclohexadiene. When polymerization was carried out with cooling $(-20^{\circ}C)$, the yield of polymer increased to 60%.

CONCLUSIONS

The reagents used were prepared and purified as described in [3] (I) and [8] (II). Spectrophotometric and kinetic studies were carried out in thermostated cells in a Specord UV-VIS instrument. The activation energy of the cation-radical of (II) was calculated from the dependence of the initial rates of formation of the phenothiazine radical on temperature (Fig. 3). The rate of decomposition of (I) and the half-wave electrochemical reduction potentials of the electron acceptors were measured at 20°C on an ON-102 instrument, base electrolyte 0.05 N Et₄N⁺I⁻ in DMF, using a three-electrode cell.

<u>Reaction of (I) with (II)</u>. 1) To a solution of 5.4 g (0.3 mole) of (II) in a mixture of THF and methanol (1:3) was added dropwise at -10° C over 4 h a solution of 6 g (0.3 mole) of (I). The solvent was removed from the reaction mixture. The fraction bp 10-20°C was found

to contain MeOH-CH₂ (GLC, Chromaton LKhM-8MD, katharometer detector, column 2.5 m \times 3 mm, 5% silicone DS-550 on Chromaton N-AW-DMS, 45°C, carrier gas helium, flow rate 25 ml/sec). The solid residue was subjected to column chromatography to give: with benzene, phenothiazine (mp 182°C, 90% yield), and with acetone, benzoic acid (mp 121°C, yield 20%).

2) Reaction of equimolar amounts (0.3 mole) of (I) and (II) in THF at 60°C in an ampul gave $PhCO_2CH=CH_2$ (46%, n_D 1.5243 [10]), 3,10-biphenothiazine (15%, mp 196-197°C [6]), and phenothiazine (40%).

3) To a solution of 5.4 g (1.2 mole) of (II) in 20 ml of toluene was added dropwise a solution of 6 g (1.25 mole) of (I) in 20 ml of toluene. The reaction was carried out for 3 h at 20°C while argon was bubbled continuously through the reaction mixture, the exhaust gas being passed through a cooled (- 70°C) spiral trap. Mass spectroscopy (MAT-212) of the condensation products showed the presence of 1,3-cyclohexadiene, m/z 78 (M⁺). The contents of the flask were concentrated and chromatographed on a column of silica gel L 100/160 to give phenothiazine, mp 181-182°C (42%), 3,10-biphenothiazine, mp 196-197° (7%) (with 1:10 and 1:1 benzene-hexane respectively), and 3-benzoylphenothiazine, mp 139-140°C, with 3:2 benzene-hexane C78.9; H 4.6; S 11.4%; $C_{19}H_{13}NSO_2$. Calculated: C 79.2; H 4.8; S 11.1%.

<u>Polymerization of (II)</u>. Polymerization was carried out in ampuls, the contents of which were degassed in vacuo $(1.33 \cdot 10^{-3} \text{ Pa})$ with freezing. A solution of (II) (1 mole) in toluene was mixed with a solution of (I) (10^{-2} mole) in a container, and kept for 24 h at 60°C. The solid which separated was filtered off, washed with hot methanol, and dried in vacuo. The yield of poly(10-vinylphenothiazine) was 10%, softening point 282-300°C. Precipitation of the mother liquors with hexane gave a benzoate-containing oligomer, softening point 135-160°C, M_n 1600-2800 (isopiestic). The IR spectrum of the material showed absorption at 1250 (COC) and 1720 cm⁻¹ (C=O). At -20°C, poly(10-vinylphenothiazine) was obtained in 60% yield . Found: S 14.1%. (C₁₄H₁₁NS). Calculated: S 14.2%.

CONCLUSIONS

The reaction of 10-vinylphenothiazine with benzoyl peroxide proceeds via the formation of a donor-acceptor complex, and breakdown of the resulting ion-radical pairs into ionic and radical components, thus allowing recombination, neutralization, initiation, and fission of the polymer chain to occur.

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