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THE KINETICS OF RADICAL POLYMERIZATION—XXVII INVESTIGATION OF THE RADICAL REACTIVITY OF 3,3'- AND 4,4'-DISUBSTITUTED AZOBENZENES IN THE POLYMERIZATION OF VINYLACETATE

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Abstract—A study was made on the inhibition by some 3,3'- and 4,4'-disubstituted azobenzenes of the polymerization of vinylacetate initiated by azoisobutyronitrile at 50°. The inhibitory effects of these substances can be attributed to their ability to engage in radical addition giving a less reactive hydrazyl type radical. The mechanism of the inhibition has been established by ESR and kinetic (stoichiometric) measurements. The value of k_5/k_2 (characteristic of the reactivity of an inhibitor) was determined for 9 substituents. The radical reactivity of the aromatic azo group was decreased by electron donor substituents and increased by electron acceptors. The substituent effect can be well interpreted by the Hammett equation; the value of the reaction constant was $\rho = +0.53$.

The inhibiting and retarding effects of aromatic azo compounds have been observed for radical polymerization of several monomers, e.g. styrene [1–3], isoprene [4], vinylacetate [5, 6], vinyl chloride [6] and methyl methacrylate [6, 7]. Not much is yet known, however, about the efficiencies of azo compounds in radical polymerization, the mechanism of inhibition and the relationship between structure and reactivity.

In order to answer these questions at least partially, we studied the effects of 3,3'- and 4,4'-disubstituted azobenzenes on the polymerization of vinylacetate initiated by azoisobutyronitrile. This paper refers to kinetic investigations of these systems and deals with the relationship between the structures of the investigated azobenzenes and their reactivities.

EXPERIMENTAL

Kinetic measurements were carried out dilatometrically at 50°. The experimental methods and the purifications of initiator (azoisobutyronitrile) and monomer (vinylacetate) have been described [8]. ESR measurements were performed by a JEOL-JES-Me 3X spectrometer.

4,4'-Dimethyl azobenzene, 3,3'-dibromo azobenzene, 4,4'-dibromo azobenzene and 4,4'-dicarboethoxy azobenzene were prepared from the corresponding diazotized amines by boiling with cuprous salt [9]. The melting points were respectively 144, 125–126, 205 and 145–146°.

3,3'-Dichloro azobenzene was prepared by reduction with iron powder at 200–300° of the corresponding azoxyderivative obtained, by reduction with zinc-powder in alkaline medium, from 3-nitro-chlorobenzene. It was recrystallized from ethanol, m.p. 125–126°.

3,3'-Dicyano azobenzene was prepared thus: 3-aminobenzonitrile (2.4 g) and nickel peroxide (17 g) were boiled in 50 ml benzene on a water bath for 6 hr; the solution was filtered while hot. After evaporation of the solvent, the residue was recrystallized three times from acetone (m.p. 162–163°). 4,4'-Dicyano azobenzene was prepared similarly. It was recrystallized twice from glacial acetic acid, then chromatographed on alumina (m.p. 269°).

2,4,6-Tricarbomethoxy hydrazobenzene was prepared thus: 5.9 g trimethyl ester of 2-fluoro trimesinic acid [10] and 10 g freshly distilled hydrazine were dissolved in 100 ml absolute methanol; the solution was kept at room temperature for 6 hr. After filtering off the precipitated phenylhydrazine-hydrofluoride, the solution was evaporated to one-third of its original volume, and then cooled. After recrystallization three times from ethanol, the precipitated white crystalline product melted at 161°. Yield: 20%. Analysis: Calc.: C, 60.32; H, 5.07; N, 7.81. Found: C, 60.40; H, 5.00; N, 7.78.

2,4,6-Tricarbomethoxy azobenzene was prepared thus: 2,4,6-tricarbomethoxy-hydrazobenzene (5 g) dissolved in 50 ml methanol was boiled with HgO (10 g) for 5 hr, filtered while hot, and the precipitate was washed with methanol. The orange coloured solution was evaporated to small volume and then cooled. The product was purified by recrystallization from petroleum ether (m.p. 115°). Yield: 90%. Analysis: Calc.: C, 60.66; H, 4.53; N, 7.86. Found: C, 60.55; H, 4.65; N, 7.91.

RESULTS

As expected, all the azobenzene derivatives inhibited the polymerization of vinylacetate. Figure 1 shows conversion vs time curves of a typical series with increasing 3,3'-dibromo azobenzene concentrations.

For all the substances investigated, inhibitor consumption was followed by gradual fading of the colour characteristic of azobenzene derivatives; after the inhibition period, the rate of polymerization reached that of the non-inhibited process. Kinetic data are interpreted by the rules of "simple inhibition" [11–13] and the kinetic parameters so obtained are summarized in Table 1.

The excellent linearity of the relationship

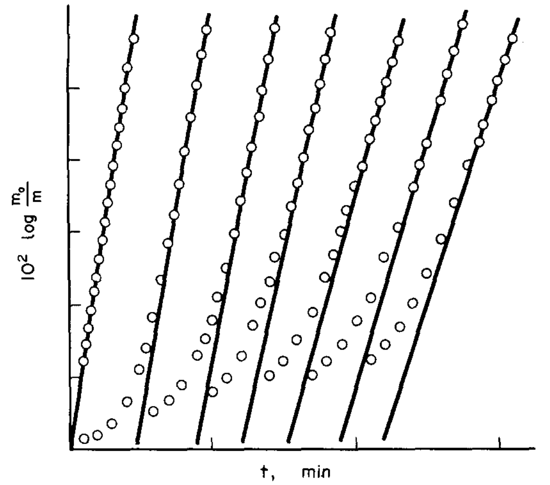


Fig. 1. Kinetic curves of polymerization of vinylacetate inhibited by 3,3′-dibromo azobenzene at 50°.

$t_i = f(z_0/\bar{x})$ shown in Fig. 2 proves the absence of side-reactions as well as the applicability of equations describing simple inhibition [26].

From the slopes of the $t_i = f(z_0/\bar{x})$ relationship (with knowledge of the rate constant of initiation [8]), the stoichiometric coefficient (μ) of inhibition was determined. Values, together with the k_5/k_2 ratios characteristic of the reactivity of inhibitors (k_5 is the rate constant of radical addition to the inhibitor and k_2 is that of chain propagation) are also listed in Table 1.

Evaluation of results

The reactivity data in Table 1 show that disubstituted azobenzenes are rather effective inhibitors in the radical polymerization of vinylacetate. Their efficiency is increased by electron acceptor substituents and decreased by electron donors. We have dealt with quantitative description of the correlation between substituent effect and radical reactivity, studying the reaction between para and meta substituted nitrobenzenes and the poly(vinylacetate) radical [14–17]. With these investigations we proved that radical reactions can be satisfactorily described by the Hammett–Taft equations [18–20]:

$$\log \frac{k_p}{k^0} = \rho(\lambda\sigma_I + \sigma_R)$$

$$\log \frac{k_m}{k^0} = \rho(\sigma_I + \alpha\sigma_R)$$

where σ_I and σ_R are inductive and mesomer components of the substituent constant, while λ and α "relative intensities" of the inductive and mesomer effects for substituents in para and meta positions resp.

The inductive constants determined during investigations with different reactions [20–22] give a common scale and can therefore be considered to a first approximation as constants independent of the reaction type. The mesomer interaction, however, depends on the mesomer effect of both the reaction centre and the substituent i.e. it depends on the type and conditions of the reaction.

Investigations of substituted azo compounds were carried out under conditions analogous to those for the nitrobenzenes.

In the description of the reactivity data (Table 2), we also assumed the validity of Hammett–Taft equations; in the calculation of σ_p and σ_m, we used λ, α and σ_R values obtained in the case of substituted nitrobenzenes, assuming similar conjugation conditions in the transition states of both reactions. The results obtained for radical reactivities of 3,5-disubstituted nitrobenzenes prove that additivity is valid in these cases [24]. Thus, in the description of the radical reactivity of azobenzenes, the following relationships were applied:

$$\log \frac{k_p}{k^0} = \rho \sum \sigma_p \qquad \log \frac{k_m}{k^0} = \rho \sum \sigma_m.$$

The experimental reactivity data plotted according to this relationship are shown in Fig. 3.

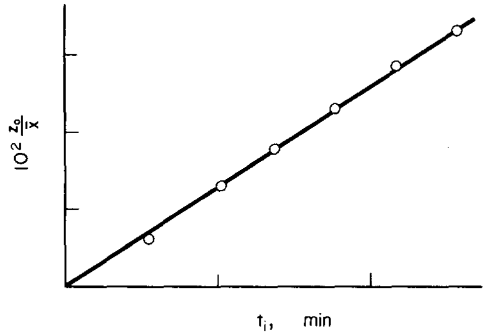


Fig. 2. Dependence of inhibition time on the concentration of inhibitor (3,3′-dibromo azobenzene).

Table 1. Kinetic data of the system vinylacetate/AIBN/substituted azobenzene/50°

Substituent	Initiator concentration (x_0 10^3 mol/dm^3)	Inhibitor concentration (z_0 10^5 mol/dm^3)	Number of experiments	Relative reactivity of inhibitors (k_5/k_2)	Stoichiometric coefficient (μ)
—H	7.86–9.80	6.28–20.93	5	28.42	1.81
—4,4′-di-CH_3	8.53–10.40	8.62–29.54	5	17.26	1.92
—3,3′-di-Br	7.72–10.56	1.50–14.44	6	71.74	1.93
—4,4′-di-Br	8.60–10.76	3.38–13.75	6	42.06	2.05
—3,3′-di-Cl	8.65–10.66	4.34–25.26	6	72.72	2.09
—4,4′-di-Cl	8.90–10.89	4.84–19.76	6	41.71	2.17
—4,4′-di-$COOC_2H_5$	8.97–9.48	4.80–16.00	6	100.50	2.06
—4,4′-di-CN	8.53–9.14	9.42–18.70	3	189.07	1.71
—3,3′-di-CN	7.64–10.55	5.26–21.88	6	103.18	1.77

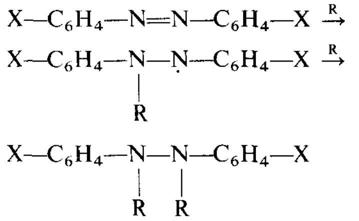
Table 2. Reactivity data of disubstituted azobenzenes

Substituent	$k_5/k_2 = k$	$\log k/k^0$	$\sigma_{(p,m)} = \log K/K^{0*}/\rho_{\text{nitro}}$
—3,3′-di-Br	71.74	0.401	0.346
—4,4′-di-Br	42.06	0.169	0.148
—3,3′-di-Cl	72.72	0.407	0.371
—4,4′-di-Cl	41.71	0.165	0.150
—4,4′-di-$COOC_2H_5$	100.50	0.547	0.496
—3,3′-di-CN	103.18	0.559	0.537
—4,4′-CN	189.07	0.821	0.738
—4,4′-di-CH_3	17.26	−0.218	−0.210
—H	28.42	0.0	0.0

* Where $K = k_5/k_2$ (subst. nitrobenzene), $K^0 = k_5/k_2$ (nitrobenzene).

The excellent correlation indicates the validity of the assumptions. From the slope of the line, $\rho = +0.53$.

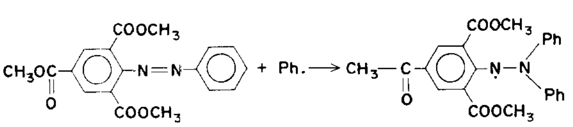
From the data of Table 1 relating to μ (number of radicals deactivated by one inhibitor molecule) it can be seen that in most cases it is, within experimental error, equal to the expected value. The absence of stoichiometric anomalies can be attributed to the fact that the intermediate radicals are sterically shielded. The value $\mu = 2.0$ means that a simple two-step inhibition occurs, represented thus



$$X{-}C_6H_4{-}N{=}N{-}C_6H_4{-}X \xrightarrow{R}$$
$$X{-}C_6H_4{-}\underset{\displaystyle R}{\underset{|}{N}}{-}\dot{N}{-}C_6H_4{-}X \xrightarrow{R}$$
$$X{-}C_6H_4{-}\underset{\displaystyle R}{\underset{|}{N}}{-}\underset{\displaystyle R}{\underset{|}{N}}{-}C_6H_4{-}X$$

where X represents the substituents in *meta* and *para* positions and R the poly(vinylacetate) radical.

In order to prove the mechanism of the inhibition reaction as well as the correctness of the assumed structures of intermediate radicals, further experiments have been carried out by the ESR technique. These investigations have been made with phenyl radicals formed in the thermal decomposition of benzoyl peroxide in benzene at 20°. For the experiments, 2,4,6-tricarbomethoxy azobenzene has been synthesized; it is believed to give a α,α-diphenyl-β-(2,4,6-tricarbomethoxyphenyl)-hydrazyl upon addition of a phenyl radical:



This radical was prepared by Braun *et al.* [25]. The ESR spectrum of the radical obtained from 2,4,6-tricarbomethoxy azobenzene upon addition of a phenyl radical is shown in Fig. 4.

For nitrogen atoms the spectrum gave the following coupling constants:

$a_N^\alpha = 6.00 \pm 0.02$ gauss,
$a_N^\beta = 11.14 \pm 0.05$ gauss.

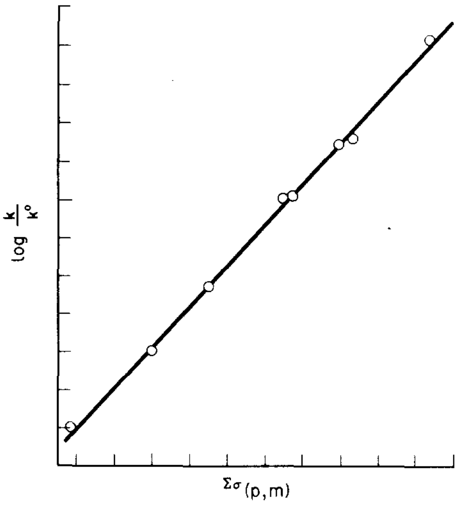


Fig. 3. Investigation of relationship between reactivity and structure for substituted azobenzene.

Since the hyperfine splitting in the ESR spectrum of the radical obtained from 2,4,6-tricarbomethoxy azobenzene and the coupling constants of nitrogen atoms are in good agreement with the corresponding published data of the α,α-diphenyl-β-(2,4,6-tricarbomethoxyphenyl)-hydrazyl radical, the radicals prepared by the two methods can be regarded as identical. Thus, it is obvious that the stable free radical can only be formed from the azo compound by 1,2-type radical addition. The intermediate product of radical addition could be observed by the ESR-method also in the case of 4,4′-disubstituted azobenzene. Figure 5 shows the ESR spectrum of the radical formed by

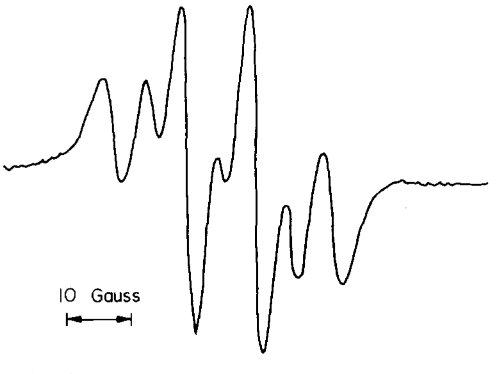


Fig. 4. ESR spectrum of N′-2,4,6-tricarbomethoxy-phenyl-*N,N*-diphenylhydrazyl.

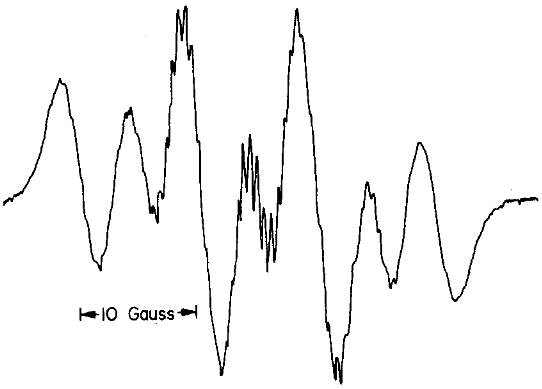


Fig. 5. ESR spectrum of the radical obtained from 4,4′-dicarboethoxy azobenzene upon addition of phenyl radical.

phenyl radical addition to 4,4′-dicarboethoxy azobenzene.

Coupling constants values for nitrogen are:

$$a_N^{\alpha} = 5.35 \pm 0.02 \text{ gauss},$$
$$a_N^{\beta} = 10.52 \pm 0.05 \text{ gauss}.$$

The spectrum consists of seven lines; in this case also, the ratio of nitrogen coupling constants is near 1:2. Further hyperfine splitting is caused by the hydrogen atoms of the *p*-carboethoxy phenyl group bonded to the nitrogen atoms of higher spin density; the coupling constants, however, cannot be measured with sufficient accuracy. Radical addition of 4,4′-dicarboethoxy azobenzene occurs with equal probability on each nitrogen atom because of the symmetrical electron structure of the molecule, while in the case of the asymmetrically substituted 2,4,6-tricarbomethoxy azobenzene which, in addition, contains a sterically shielded nitrogen atom, the first radical addition step is mainly preferred.

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