2. In distinction to the monofunctional aromatic amines and phenols, the antioxidant activity of the pphenylenediamine derivatives increases as the oxygen pressure is reduced.

 $3. \ \ {\rm The \ p-phenylenediamine \ derivatives \ do not \ show \ synergistic \ effects \ when \ mixed \ with \ alkyl-radical \ acceptors.$

4. The inhibiting action of the p-phenylenediamines can be explained by assuming these compounds to form autosynergistic mixtures with their reaction products, quinonediimines, capable of reacting with alkyl radicals.

LITERATURE CITED

- 1. L. I. Belova, G. V. Karpukhina, Z. K. Maizus, É. G. Rozantsev, and N. M. Émanuél', Dokl. Akad. Nauk SSSR, 231, 369 (1976).
- 2. L. I. Mazaletskaya, G. V. Karpukhina, and Z. K. Maizus, Neftekhimiya, 19, 214 (1979).
- 3. L. N. Denisova, E. T. Denisov, and D. I. Metelitsa, Zh. Fiz. Khim., 44, 1670 (1970).
- 4. G. V. Karpukhina, Z. K. Maizus, and M. Ya. Meskina, Kinet. Katal., 9, 245 (1968).
- 5. G. V. Karpukhina, Z. K. Maizus, and L. I. Matienko, Neftekhimiya, 6, 603 (1966).
- 6. N. A. Azatyan, T. V. Zolotova, G. V. Karpukhina, and Z. K. Maizus, Neftekhimiya, 11, 569 (1971).
- 7. N. M. Émanuél', E. T. Denisov, and Z. K. Maizus, Chain Reactions in Liquid-Phase Hydrocarbon Oxidations [in Russian], Nauka, Moscow (1965), p. 4.
- 8. L. I. Belova and G. V. Karpukhina, Izv. Akad. Nauk SSSR, Ser. Khim., 1740 (1977).
- 9. B. V. Pavlov and A. Ya. Povzner, Zh. Vychisl. Matem. Matem. Fiz., 13, 1056 (1973).
- 10. L. I. Mazaletskaya, G. V. Karpukhina, and Z. K. Maizus, Izv. Akad. Nauk SSSR, Ser. Khim., 1981 (1981).
- 11. K. B. Piotrovskii and Yu. A. L'vov, Dokl. Akad. Nauk SSSR, 198, 122 (1971).
- 12. L. G. Privalova, L. D. Tyutchenkova, S. P. Kirichenko, and Z. K. Maizus, Izv. Akad. Nauk SSSR, Ser. Khim., 1042 (1972).
- 13. G. Scott and K. Smith, Europ. Polym. J., 14, 39 (1978).
- 14. K. A. Zolotareva, I. P. Maslova, V. M. Delyusto, et al., Boosters for Polymeric Materials [in Russian], Khimiya, Moscow (1966), p. 17.

COMPARATIVE REACTIVITY OF α -ACETOXYACROLEIN

AND α - ETHOXYACROLEIN

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 α -Acetoxyacrolein (I) [1] contains a previously unknown combination of reaction centers, geminal CHO and CH₃COO groups at a double bond. We should expect that the conjugation of the vinyl group with the ester oxygen in (I), in comparison with α -ethoxyacrolein (II) [2], should be weakened because of the influence of the neighboring electron-acceptor acetyl group.[†]

According to the IR and UV spectra (Table 1), the lower degree of conjugation in (I) is reflected by a hypsochromic shift of the $\pi \rightarrow \pi^*$ transition and an increase in the absorption frequency of the C = C bond and the out-of-plane deformation vibrations of the = CH₂ group.

The results from calculations of the π -electron density in (I) and (II) by the SCF MO LCAO method in the PPP variant (Fig. 1) also showed that the degree of polarization of the C = C bond is lower by a factor of nearly 2 in (I). However, the C = C bond is polarized in the same direction in both cases, in the direction of the β -carbon atom. The position and intensity of the absorption maximum thus calculated for (I) (λ_{calc} 215 nm,

†See [3] on the polarization of the double bond of vinyl acetate.

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TABLE 1. Parameters of UV and IR Spectra of (I) and (II)

Compound	$\pi \mapsto \pi^*$ transition λ , nm (log ε) (in water)	IR spectrum, ν , cm ⁻¹		
		C==C	=CH,	
$\begin{array}{c} \mathrm{CH}_{2} = \mathbb{C}\left(\mathrm{OAc}\right) \mathrm{CHO} \ (\mathrm{I}) \\ \mathrm{CH}_{2} = \mathbb{C}\left(\mathrm{OC}_{2}\mathrm{H}_{5}\right) \mathrm{CHO} \ (\mathrm{II}) \end{array}$	216 (3.85) 250 (3.89)	1643 1610	870 811	
$\begin{array}{c} -0,082 \\ -0,059 +0,010 \\ C \\ +0,059 \\ 0 \\ \end{array} \\ \begin{array}{c} -0,052 \\ -0,052 \\ -0,07 \\ +0,062 \\ C \\ -0,154 \\ -0,154 \\ -0,145 \\ \end{array} \\ \begin{array}{c} -0,071 \\ +0,060 \\ 0 \\ -0,145 \\ \end{array} \\ \begin{array}{c} -0,052 \\ -0,17 \\ -0,145 \\ \end{array} \\ \begin{array}{c} -0,071 \\ -0,052 \\ -0,17 \\ -0,145 \\ \end{array} \\ \begin{array}{c} -0,071 \\ -0,052 \\ -0,010 \\ -0,000 \\ -0,$				

Fig. 1. Molecular diagrams of distribution of π -electron density in α -ethoxyacrolein (a) and α -acetoxyacrolein (b).

 $\log \varepsilon 3.61$) coincide with the values actually found (Table 1). Chemical confirmation of the direction of polarization of the C = C bond in (I) is found in the formation of the corresponding bishydrazone (III) and bisthiosemicarbazone of methylglyoxal (IV) upon interaction of (I) with 2,4-dinitrophenylhydrazine and thiosemicarbazide,

$$(I) + H_2O \xrightarrow{H^+} [CH_3COCHO]$$

$$TSC \qquad \qquad 2.4-DNPH$$

$$\downarrow CH_3CCH=NNHCSNH_2 \qquad CH_3CCH=NNHC_6H_3(NO_2)_2$$

$$\parallel NNHCSNH_2 (IV) \qquad NNHC_6H_3(NO_2)_2 (III)$$

The interaction of (I) with 3,5-dinitrobenzoylhydrazide in the absence of acid leads to the unsaturated azomethine derivative (V) (without the participation of the vinyloxy group),

$$(I) + H_2NNHCOC_6H_3(NO_2)_2 \rightarrow CH_2 = C(OCOCH_3)CH = NNHCOC_6H_3(NO_2)_2 \quad (V)$$

A quantitative confirmation of the weaker polarization of the C = C bond in (I) can be found in the results from a kinetic study of the hydrolysis of (I) and (II). In contrast to (II), we found that it was impossible to carry out kinetic measurements on (I) in water, since when it was dissolved in water, a precipitate was formed. This precipitate, judging by its elemental analysis and IR spectrum, is a polymer of (I). An analogous phenomenon has been described for an α -cyanoacrylate [4]. Because of this behavior, we studied the hydrolysis of (I) in a water / acetonitrile medium, where no polymer formation was observed. The constants k_1 and k_2 were determined from the formulas

$$k_1 = \frac{1}{t} \cdot 2.303 \lg \frac{D_0}{D_t}$$
 $k_2 = \frac{k_1}{[\text{HCl}]}$

Within the range of acidities investigated (0.01-0.1 mole/liter), the rate constant k_1 for the hydrolysis of (II) varies linearly with the concentration of catalyst (r = 0.9782, based on five measurements). As can be seen from Table 2, the hydrolysis of (I) in an acidic medium is 10 times slower than the hydrolysis of (II). The addition of acrylonitrile to the aqueous solution of (II) lowers its hydrolysis rate by almost an order of magnitude.

EXPERIMENTAL

The IR spectra were obtained in a UR-20 instrument. The UV spectra and the kinetics of hydrolysis were investigated in a Specord UV-VIS spectrophotometer in thermostated cuvettes (1.0 and 0.1 cm). The course of the reaction was followed according to the drop in the absorption maximum at 250 nm (II) or 216 nm (I). The hydrolysis of (II) was carried out in an aqueous medium at 25° and 35°C and in a H_2O/CH_3CN medium (1/1) at 35°C. The substrate concentration was 0.00015 mole/liter, and the concentration of catalyst (HCl) was 0.01-0.1 mole/liter. The hydrolysis of (I) was carried out in a H_2O/CH_3CN medium (1/1) at 35°C; the substrate concentration was 0.00075 mole/liter, and the HCl concentration was 0.2-0.4 mole/liter. The required quantities of the substrate and catalyst solutions were thermostated and then mixed, at which point the timing

TABLE 2. Rate Constants for Hydrolysis of (I) and (II), $k_2\cdot 10^2$, liters/mole·sec

Solvent	(I)	(II)	
	35°	25°	35°
H_2O H_2O-CH_3CN (1 : 1) H_2O-CH_3CN (1 : 2)	$[0,052\pm0,03\\0,030\pm0,02]$	1,538±0,033	3,49±0,03 0,42±0,16

of the experiment was started, and the timewise change in optical density was recorded. The UV spectrum of the final product has an absorption maximum at 287 nm.

Interaction of α -Acetoxyacrolein with 3,5-Dinitrobenzoylhydrazide. To 0.2 g of (I), 0.2 g of 3,5-dinitrobenzoylhydrazide in 30 ml of ethanol was added, and the mixture was heated for 10 min at 60°C. After cooling, 0.25 g (50%) of (V) precipitated, mp 195°C (from ethanol). Found: C 44.55%; H 3.00%; N 17.28%. $C_{12}H_{10}O_7N_4$. Calculated: C 44.5%; H 3.14%; N 17.4%.

Interaction of α -Acetoxyacrolein with 2,4-Dinitrophenylhydrazine. A mixture of 0.22 g of (I), 0.76 of 2,4-dinitrophenylhydrazine, 75 ml of alcohol, and two drops of concentrated HCl was heated for 15 min at 60°C. Upon cooling, 0.3 g (45%) of (III) precipitated, mp 320°C (from nitrobenzene). A mixed test with a known sample did not give any depression of the melting point.

Interaction of α -Acetoxyacrolein with Thiosemicarbazide. A mixture of 0.5 g of (I), 0.4 g of thiosemicarbazide, 25 ml of water/ethanol mixture (1/2) and one drop of concentrated HCl was heated for 15 min at 60°C. Upon cooling, 0.5 g (50%) of (IV) precipitated, mp 230°C (from DMFA). Found: N 37.16%; S 29.57%. C₅H₁₀N₅S₂. Calculated: N 38.85%; S 29.35%. A mixed test with a known sample did not give any depression of the melting point.

CONCLUSIONS

1. The rate of hydrolysis of α -acetoxyacrolein in an acid medium is an order of magnitude lower than that of α -ethoxyacrolein. The formation of methylglyoxal as a result of the hydrolysis of α -acetoxyacrolein along with a calculation of the π -electron density of this compound by means of the SCF MO LCAO method, indicates delocalization of the π -electrons of the C = C bond in α -acetoxyacrolein in the direction of the β carbon atom.

2. In the reaction of α -acetoxyacrolein with 2,4-dinitrophenylhydrazine, thiosemicarbazide, and 3,5dinitrobenzoylhydrazide, either monoazomethine or bisazomethine derivatives may be formed, depending on the acidity of the medium.

LITERATURE CITED

- 1. N. A. Keiko, T. N. Musorina, I. D. Kalikhman, and M. G. Voronkov, Zh. Obshch. Khim., <u>49</u>, 170 (1979); USSR Inventor's Certificate 694,493, Byull. Izobret., No. 40 (1979).
- 2. M. F. Shostakovskii, N. A. Keiko, A. P. Chichkarev, and O. N. Vylegzhanin, Izv. Akad. Nauk SSSR, Ser. Khim., 2715 (1971).
- 3. A. F. Rekasheva, Usp. Khim., <u>37</u>, 2272 (1968).
- 4. Vestn. Akad. Nauk SSSR, 3 (1980).