KINETICS AND PRODUCTS OF THE REACTION OF DIAZO COMPOUNDS WITH SO_2

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Data were obtained on the composition of products and kinetics of the reaction of SO_2 with $Ph(R)CN_2$ (R = Ph, Me) in solutions of isooctane, 1,4-dioxane, and ethanol at 295 K. A mechanism was proposed for the process in accordance with which the sulfene being formed participates in concurrent reactions with the starting reagents. The relative rate constants for the process stages were determined.

Reaction of diazo compounds with SO_2 is a potential source for obtaining such intermediates as sulfenes. Some aspects of this reaction appear in [1, 2]. In this work the kinetic features of the reaction of diphenyldiazomethane with SO_2 as well as the composition of the reaction products of diphenyl- and phenylmethyldiazomethane with SO_2 were studied.

EXPERIMENTAL

Synthesis and purification of diphenyldiazomethane (DPDM) and phenylmethyldiazomethane (PMDM) were carried out by the methods of [3, 4], respectively. Isooctane was purified in H_2SO_4, after which it was distilled in an Ar atmosphere. Methanol, ethanol, cyclohexanol, and 1,4-dioxane were purified according to [5]. Acetonitrile was purged with a mixture of O_3 and O_2, then with Ar and distilled over P_2O_5.

The reaction kinetics of DPDM with SO_2 were studied spectrophotometrically with respect to substrate consumption. A solution of SO_2 was placed in a hermetically sealed quartz cuvette (optical path length 0.5 cm) then a solution of DPDM in the same solvent was added and the change in absorbance at $\lambda = 525$ nm was recorded in the automatic mode.

The content of diazo compounds, SO_2, and benzophenonazine (BPA) was determined spectrophotometrically. At $\lambda = 290$ nm the extinction coefficient of SO_2 in isooctane $\varepsilon(SO_2)_{290} = 290$ liters/(mole·cm) [6]. The extinction coefficient of SO_2 in ethanol $\varepsilon(SO_2)_{276} = 600$ liters/(mole·cm) and in 1,4-dioxane $\varepsilon(SO_2)_{276} = 960$ liters/(mole·cm) were measured by reference to the absorbance of SO_2 in isooctane. The extinction coefficients of DPDM and PMDM in isooctane, ethanol, and 1,4-dioxane were determined by adding an excess of benzoic acid to the solution of diazo compounds and the excess titrated with tetrabutylammonium hydroxide: $\varepsilon(DPDM)_{525} = 130 \pm 10$ liters/(mole·cm) and $\varepsilon(PMDM)_{510} = 36 \pm 3$ liters/(mole·cm).

Benzophenone (BP) was analyzed via GLC (150-200°C, 10% SE-30 on a Chromatone N-AW).

The relative content of products of the reaction of PMDM with SO_2 was determined by ^1H NMR on a Tesla-567 spectrometer.

RESULTS AND DISCUSSION

Kinetics of the Process. Typical kinetic curves for the consumption of DPDM are shown in Fig. 1. The rate constants for the second order reaction

$$k_{\text{exptl}} = W_0/[SO_2]_0 \cdot [\text{DPDM}]_0 \tag{1}$$

were calculated from them, where W_0 is the initial reaction rate and $[SO_2]_0$ and $[DPDM]_0$ are the concentrations of the reagents in the starting mixture.

In order to determine k_{exptl} the initial portions of these kinetic curves were approximated by the function $[DPDM] = [DPDM]_0 \times \exp(-\alpha t)$, where a is a parameter that varies

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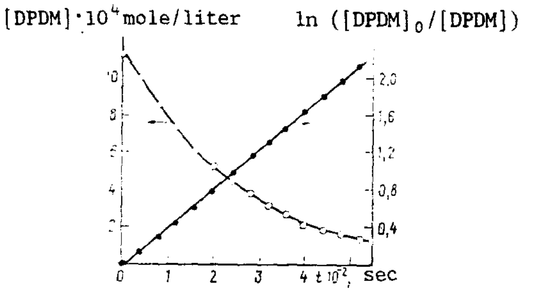


Fig. 1

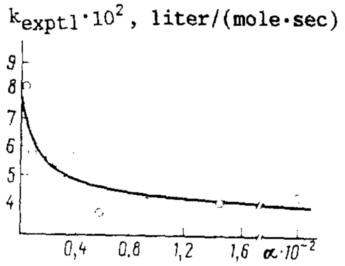


Fig. 2

Fig. 1. Kinetic curves of DPDM (1) consumption and its semilogarithmic anamorphosis (2) (isooctane, $[SO_2] = 0.1$ mole/liter, 295 K.

Fig. 2. k_{exptl} vs α. Solid line obtained by optimization (last value on the x-axis 2.4).

TABLE 1. Dependence of the Rate of the Reaction of DPDM with SO_2 on the Nature of the Solvent and Additions of Alcohol (295 K)

Solvent	Alcohol R—OH	[ROH], mole/liter	$k_{exptl}\cdot 10^2$, liter/(mole·sec)
Isooctane	CH_3OH	0	3,9
		0,02	5,9
		0,2	11,8
	cyclo-$C_6H_{11}OH$	0,2	5,7
		2,0	29,2
1,4-Dioxane	C_2H_5OH	0	4,0
		0,7	16,1
		1,0	25,3
		1,7	33,1
Ethanol	–	–	180

in the range 10^{-4} - 10^{-1} sec^{-1}. We note that for $\alpha = [SO_2]_0/[DPDM]_0 > 10$ the kinetic curves are linearized in the coordinates $\ln([DPDM]_0/[DPDM])$—t to a depth of conversion of 70-90% and for $\alpha \simeq 0.5$-2 to 10-30%. Values of k_{exptl} were calculated from the formula $k_{exptl} = \alpha/[SO_2]_0$.

Figure 2 shows k_{exptl} vs α. For $\alpha \to 0$ and $\alpha \to \infty$ k_{exptl} converges to the limiting values $2k_0$ and k_0, respectively. The value of the effective rate constant changes little when isooctane is replaced by 1,4-dioxane. However, when alcohols are added k_{exptl} increases markedly. Carrying out the reaction in an EtOH medium leads to an increase in k_{exptl} of more than 40 times (Table 1), which probably is explained by SO_2 forming complexes with the alcohols [7-9].

PMDM is significantly more active with respect to SO_2 than DPDM: for $[PMDM]_0 = [SO_2]_0 = 5\cdot 10^{-3}$ mole/liter the time of semiconversion $\tau_{1/2} \le 2$ sec and, consequently, $k_{exptl} \ge 10^2$ liter·mole⁻¹·sec⁻¹.

Composition of Products of Reactions of DPDM and PMDM with SO_2. The chief reaction products of DPDM with SO_2 in isooctane are BP and BPA. The first of these was separated from the reaction mixture (after removal of solvent and SO_2) in experiments with $\alpha = 100$. BP was identified by ^1H NMR, IR, and electronic spectroscopy. For separation and identification of BPA the reaction was carried out at $\alpha = 0.5$. The spectral properties of BPA were: UV spectrum (isooctane): $\lambda_{max} = 278$ nm ($\varepsilon = 2\cdot 10^4$), 313 nm ($\varepsilon = 1.6\cdot 10^4$); IR spectrum ($\nu$, cm^{-1}, mineral oil): 1330, 1390, 1470 (Ph), 1590 (C=N); ^1H NMR spectrum (δ, ppm, $(CD_3)_2CO$): 7.32-7.28m (Ph). The relative BP and BPA content depends on $[SO_2]$; as $[SO_2]$ grows the fraction of BPA drops and BF increases (Table 2). For $\alpha > 39$ the BP yield ≥ 86%.

Introduction of MeOH into the system DPDM—SO_2—isooctane leads to a decrease in the yield of BP and BPA owing to formation of methyldiphenylmethanesulfonate (MS) (Table 2). Ethyldiphenylmethanesulfonate was separated from the system DPDM ($2.6\cdot 10^{-3}$ mole/liter)—SO_2 (10^{-3} mole/liter)—ethanol. IR spectrum (ν, cm^{-1}, mineral oil): 935, 1010, 1175, 1350 (SO_2), 1465 (Ph). ^1H NMR spectrum (δ, ppm, C_6D_6): 7.58-7.49m, 7.16-7.01m (Ph), 5.38s (CH), 3.79-3.59q (CH_3), 0.76-0.62t (CH_2).

TABLE 2. Dependence of Composition of Reaction Products of DPDM with SO_2 on the Initial Concentration of Reagents (mole/liter) in Isooctane at 293 K

$[DPDM]_0 \cdot 10^3$	$[SO_2]_0 \cdot 10^2$	α	$[CH_3OH]_0$	Yield, mole %		
				[BP]	[BPA]	[MS]
13,0	0,65	0,5	–	19	40	–
6,8	6,2	0,9	–	22	33	–
4,3	2,9	6.9	–	82	9	–
1,8	3,5	19,4	0,02	60	9	21
2,4	3,5	14,6	0,2	54	9	27
5.0	10,0	20,0	12,5 *	9	–	90 **
2,8	11,0	39,2	–	86	7	–
1,9	11,0	57	–	90	5	–
1,1	10,0	91	–	86	7	–
1,1	16,0	145	–	93	3	–

*Solvent C_2H_5OH.
**Ethylsulfonate.

TABLE 3. Dependence of Composition of Reaction Products of PMDM with SO_2 on the Initial Concentrations of Reagents (mole/liter) in Isooctane at 293 K

$[DPDM]_0 \cdot 10^3$	$[SO_2]_0 \cdot 10^2$	α	Yield, mole %		
			[ES]	[DPB]	[AP]
8,1	0,8	1,0	21	24	9
7,0 *	0,7	1,0	11	18	18
8,0	4,4	5,5	14	23	23
0,2	0,9	45	11	8	62
0,2	2,0	100	11	5	68
0,2	2,7	145	15	–	70

*Solvent, ethanol; ethylsulfonate is part of the composition of the products (yield 23%).

As a result of the reaction of PMDM with SO_2 in isooctane an episulfone, olefin, and a ketone accumulate; ethylsulfonate is formed in the EtOH solution (Table 3).

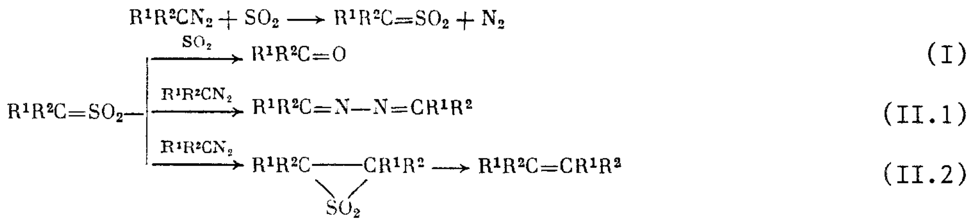
1,1-Dioxo-2,3-diphenyl-2,3-dimethylthiran—episulfone (ES) was separated in the form of a precipitate from the system $PMDM-SO_2$—isooctane and washed with hexane. UV spectrum (isooctane): $\lambda_{max} = 245$ nm ($\varepsilon = 1.4 \cdot 10^4$). IR spectrum (ν, cm^{-1}, mineral oil): 1040, 1090, 1100, 1170, 1390 (SO_2), 1470 (Ph). ^1H NMR spectrum (δ, ppm, CH_2Cl_2): 7.39-7.35m (Ph), 1.86s (CH_3).

2,3-Diphenyl-2-butene (DPB) was obtained via thermal decomposition of ES (70°C) and recrystallized from hexane. IR spectrum (ν, cm^{-1}, mineral oil): 1380, 1470 (Ph), 1610 (C=C). ^1H NMR spectrum (δ, ppm, CH_2Cl_2): 7.94-7.84m, 7.42-7.21m (Ph), 2.32s (CH_3).

Phenylmethylketone (PMK) was identified by ^1H NMR and UV spectroscopy.

Ethyl-2-phenylethanesulfonate was identified from the ^1H NMR of the products liberated from the system $PMDM-SO_2$—ethanol after removal of the solvent by exclusion of the signals from protons of ES, DPB, and PMK. ^1H NMR spectrum (δ, ppm, CH_2Cl_2): 7.34-7.21m (Ph), 4.40-4.20q (CH), 4.05-3.93q (CH_2), 1.82-1.72d (CH_3—CPh), 1.30-1.17t (CH_3—C—O).

Reaction Mechanism. Based on the results obtained the following reaction scheme is proposed



For DPDM $R^1 = R^2 = C_6H_5$; for PMDM $R^1 = CH_3$ and $R^2 = C_6H_5$.

In accord with this scheme under steady state conditions relative to the concentration of the sulfene the initial rate of consumption of the substrate is described by the following equation

$$W_0 = (-d[R^1R^2CN_2]/dt)_{t=0} = k_0[R^1R^2CN_2]_0[SO_2]_0 \times \{1 + k_2[R^1R^2CN_2]_0/(k_1[SO_2]_0 + k_2[R^1R^2CN_2]_0)\} \quad (2)$$

where $k_2 = k_{21} + k_{22}$. We note that all the rate constants (with the possible exception of k_0) are effective.

From comparison of (1) and (2) it follows that

$$k_{\mathrm{expt}} = k_0\{1 + k_2[\ \mathrm{DPDM}\ ]_0/(k_1[SO_2]_0 + k_2[\ \mathrm{DPDM}\ ]_0)\} \quad (3)$$

The results of optimizing k_{expt1} as a function of α using (3), which was carried out by the least squares method for nonlinear multiparametric regression, are shown in Fig. 2. As is seen, expression (3), and consequently (2), describes the experimental data well. As a result of optimization the following kinetic parameters were determined: $k_0 = 3.9 \pm 0.3$ [10^{-2} liter/(mole·sec)] and $k_2/k_1 = 14.3 \pm 2.3$.

The value of the ratio k_2/k_1 was also determined by an independent method from the ratio of the reaction products of (I) and (II)

$$d[R^1R^2C{=}O]/d[P_2] = k_1[SO_2]/k_2[R^1R^2CN_2] \quad (4)$$

where P_2 is the combination of the products of stages (II.1) and (II.2).

According to Table 2, when $[SO_2]_0 \gg [R^1R^2CN_2]_0$ ($\alpha \simeq 90\text{-}145$) $[R^1R^2C{=}O] \gg [P_2]$. This allows (with an error of 7-14%) description of the stoichiometric equation of the reaction

$$[R^1R^2CN_2]_0 = [R^1R^2CN_2] + [R^1R^2C{=}O] + 2[P_2]$$

in the following form

$$[R^1R^2CN_2]_0 \approx [R^1R^2CN_2] + [R_1{}^1R^2C{=}O] \quad (5)$$

After substitution of (5) in expression (4) and integration we obtain

$$k_2/k_1 = [SO_2]_0[P_2]/([R^1R^2CN_2]_0 - 0.5[R^1R^2C{=}O]) \times [R^1R^2C{=}O] \quad (6)$$

From (6), using the data of Table 2 for the reaction of DPDM with SO_2, $k_2/k_1 = 13.0$ (α = 91) and 10.5 (α = 144) was obtained. This agrees well with the results of determining this parameter from the kinetics of consumption of the substrate. The average value of k_2/k_1 lies in the range of 11.8 ± 1.2.

The value of k_2/k_1 for the reaction of PMDM with SO_2 in isooctane was determined with and error of 30-32% from the data of Table 3 and formula (6). For this reaction at 295 K, $k_2/k_1 = 41.6 \pm 5.9$ (α = 100-145).

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