Oxidation of diazo compounds by triphenyl phosphite ozonide. Quenching of singlet oxygen by diazo compounds

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The reaction of triphenyl phosphite ozonide with various types of diazo compounds results in their oxidation, which is accomplished by singlet oxygen ($^1O_2$) evolved during thermal decomposition of the ozonide. A decrease in the ionization potential of the substrate results in an increase in the overall rate constant of quenching of $^1O_2$. In the case of 9-diazofluorene, the main channel of $^1O_2$ quenching is physical quenching.

Key words: phosphite ozonides, singlet oxygen; diazo compounds; ionization potential; rate constant of quenching of singlet oxygen.

Oxidation of diazo compounds is a rather poorly investigated branch of chemistry. It has been found that triplet molecular oxygen reacts slowly with diazo compounds, and the reaction occurs with the retention of the diazo group.[1] Singlet molecular oxygen reacts rapidly with diazo compounds under mild conditions with decomposition of the diazo group.[2,3]

Phosphite ozonides $(RO)_3PO_3$, adducts of ozone with phosphites, are efficient oxidants of organic compounds. Two mechanisms of the oxidation of a substrate (A) with these ozonides are possible.[4]

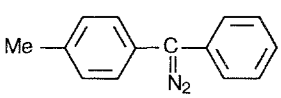
One of these involves oxidation with the singlet oxygen formed upon decomposition of $(RO)_3PO_3$.

$$(RO)_3PO_3 \longrightarrow {}^1O_2 \xrightarrow{A} AO_2$$

In the second case, direct transfer of oxygen from the ozonide to the substrate occurs, *i.e.*, the $(RO)_3PO_3$ molecule itself acts as the oxidizing reagent.

$$(RO)_3PO_3 + A \rightarrow AO_2 + (RO)_3PO$$

In the present work we studied the oxidation of (*p*-tolyl)phenyldiazomethane (**1**), diphenyldiazomethane (**2**), (*p*-chlorophenyl)phenyldiazomethane (**3**), (methyl)phenyldiazomethane (**4**), 9-diazofluorene (**5**), phenyldiazomethane (**6**), 2-diazoadamantane (**7**),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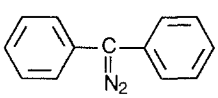
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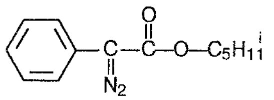
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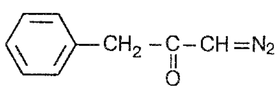
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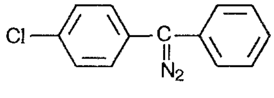
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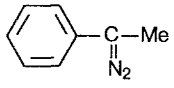
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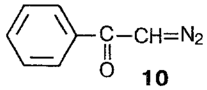
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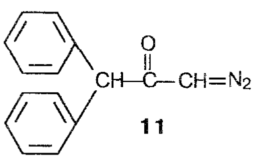
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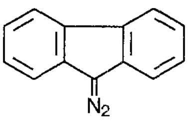
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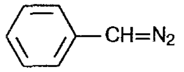
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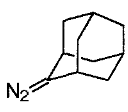
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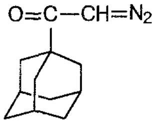
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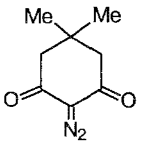
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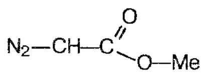
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isopentyl phenyldiazoacetate (**8**), 1-phenyl-3-diazoacetone (**9**), benzoyldiazomethane (**10**), 1,1-diphenyl-3-diazoacetone (**11**), 1-adamantanoyldiazomethane (**12**), diazodimedone (**13**), and methyl diazoacetate (**14**) with triphenyl phosphite ozonide.

Experimental

Kinetics of the reaction was studied by the chemiluminescence (CL) method[5] based on the consumption of the ozonide. 1—2 mL of a solution of a diazo compound in CH_2Cl_2 was added to a solution of $(PhO)_3PO_3$ in 20 mL of CH_2Cl_2 in a temperature-controlled (−15 °C) reactor, and the change in the CL in the IR region was recorded (Fig. 1, *a*). The concentrations of the triphenyl phosphite ozonide and the substrate were: $[(PhO)_3PO_3] \approx 1 \cdot 10^{-3}$ mol L^{-1} and $[A]_0 \approx 1 \cdot 10^{-2}$ to $6 \cdot 10^{-1}$ mol L^{-1}.

The reactivity of diazo compounds with respect to $^1O_2$ was studied by following the quenching of luminescence of $^1O_2$ in the IR region.[6] 16—20 mL of CH_2Cl_2 was placed into a temperature-controlled reactor, cooled to −15 °C, and purged with argon; 0.02 mol of $(PhO)_3PO_3$ in CH_2Cl_2 was added and the intensity of luminescence (I_0) was recorded. A cooled solution of $1—1 \cdot 10^{-4}$ mmol of diazo compound A in CH_2Cl_2 was added with intense stirring, and the intensity of chemiluminescence (I) was recorded (see Fig. 1, *a*).

A separate determination of the constants of chemical and physical quenching of $^1O_2$ was based on the stoichiometry of the consumption of the ozonide and the diazo compound, as described in the literature.[7] 1.5—1.7 mL of CH_2Cl_2 and 0.2—0.4 mL of a solution of a diazo compound ($1 \cdot 10^{-2}$—$1 \cdot 10^{-1}$ mol L^{-1}) were placed in a narrow glass reactor in the dark, and the mixture was cooled to −15 °C with temperature control. 0.2—1 mL of a solution of $(PhO)_3PO_3$ ($1 \cdot 10^{-1}$ mol L^{-1}) was added using a cooled pipet, and the reaction mixture was kept in the dark at −15 °C for approximately three half-life periods of $(PhO)_3PO_3$ (1.5 h). Then the solutions were thawed and analyzed for the content of A by spectrophotometry.

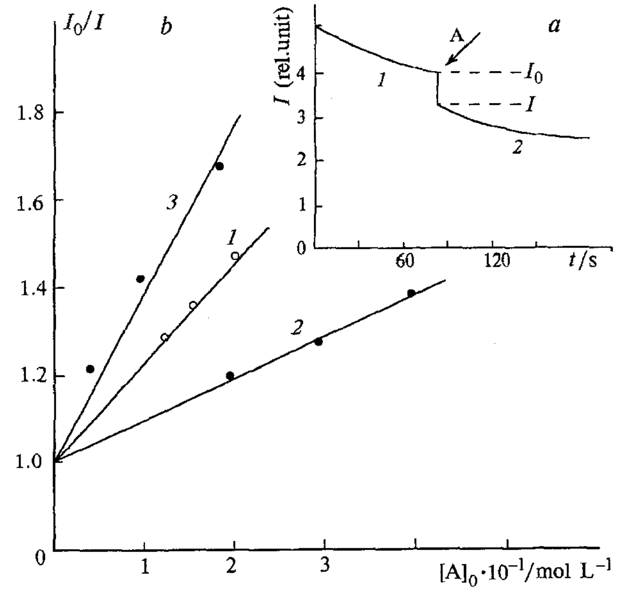


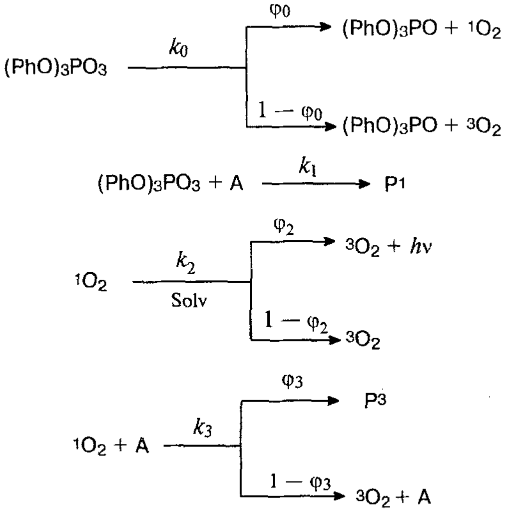
Fig. 1. *a*. The typical kinetics of the attenuation of CL during thermolysis of $(PhO)_3PO_3$ (−15 °C) in the absence (*1*) and in the presence (*2*) of the acceptor (1,1-diphenyl-3-diazoacetone), $[A]_0 = 2 \cdot 10^{-1}$ mol L^{-1}. The arrow marks the instant of the introduction of 1,1-diphenyl-3-diazoacetone. *b*. Quenching of the $^1O_2$ luminescence (−15 °C, CH_2Cl_2) in the presence of benzoyldiazomethane (*1*), 1,1-diphenyl-3-diazoacetone (*2*), and methyl diazoacetate (*3*).

Preparation of triphenyl phosphite ozonide and purification of dichloromethane were carried out by the known procedures.[8,9]

The first ionization potentials (IP_1) were determined by photoelectron spectroscopy using an ES-3201 electron spectrometer. The kinetic energy scale was calibrated using the xenon (IP_1 = 12.13 eV, IP_2 = 13.43 eV) and argon (IP_1 = 15.76 eV, IP_2 = 15.94 eV) bands. The errors in determining the maxima of the ionization bands were no more than 0.03 eV. MNDO quantum-chemical calculations carried out with full optimization of geometry in the SP basis were used for additional interpretation of the experimental data.[10]

Results and Discussion

Kinetics of the reaction. The main pathways of the consumption of $(PhO)_3PO_3$ and A can be described in the framework of the following mechanism:



Here φ_0 is the yield of $^1O_2$ (moles per mole of the consumed ozonide); φ_2 is the yield of radiation of $^1O_2$; φ_3 is the efficiency of chemical quenching of $^1O_2$ by the substrate; k_0, k_1, k_2, and k_3 are the rate constants of the corresponding reactions; P^1 and P^3 are the products of the corresponding steps.

Then

$$I = k_2 \varphi_2 [^1O_2],$$

$$-d[(PhO)_3PO_3]/dt = k_0[(PhO)_3PO_3] + k_1[(PhO)_3PO_3][A].$$

Due to the small lifetimes of $^1O_2$ in the liquid phase, the concentration of $^1O_2$ may be regarded to be steady-state.

$$[^1O_2] = \frac{k_0 \varphi_1 [(PhO)_3PO_3]}{k_2 + k_3 [A]}$$

Since $[(PhO)_3PO_3] \ll [A]_0$,

$$[(PhO)_3PO_3] = [(PhO)_3PO_3]_0 \cdot \exp\{-(k_0 + k_1[A]_0)t\}.$$

Hence, it follows that

$$\log(I_0/I) = k'/t, \quad (1)$$

where $k' = (k_0 + k_1[A]_0)$ is the effective rate constant of the consumption of the ozonide.

Equation (1) makes it possible to determine k'. From the dependence of k' on $[A]_0$, the rate constants of the thermal decomposition of $(PhO)_3PO_3$ and its interaction with the acceptor can be derived.

It was experimentally shown that at $[A]_0 \gg [(PhO)_3PO_3]_0$, the kinetics of the luminescence attenuation is described by the following equation:

$$\log(I_0/I) = k''/t. \quad (2)$$

At $k' = k''$, Eqs. (1) and (2) coincide. The effective rate constant k'' does not depend on the concentration of the substrate over the studied range of the variation of [A] (Fig. 2), and therefore, the following equation holds for the rate of ozonide consumption:

$$-d[(PhO)_3PO_3]/dt = k''[(PhO)_3PO_3].$$

Similar relationships were obtained for the other diazo compounds. The k'' constants are close to the rate constants (k_0) of the thermal decomposition of $(PhO)_3PO_3$. As shown in Fig. 2, $k'' = (3.5\pm1.0) \cdot 10^{-3}$ s^{-1}; under similar conditions, $k_0 = 2.5 \cdot 10^{-3}$ s^{-1} (see Ref. 11). The form of the kinetic equation (zero order with respect to the substrate) indicates that the direct reaction between the ozonide and the substrate does not occur, and the $^1O_2$ liberated during decomposition of the ozonide acts as the oxidizing agent.

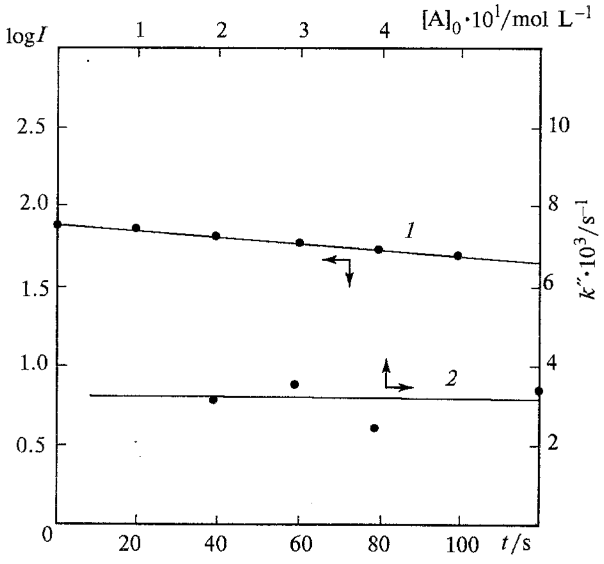


Fig. 2. The typical semilogarithmic anamorphosis of the kinetic curve of the attenuation of IR CL (*1*) during oxidation of 1,1-diphenyl-3-diazoacetone with triphenyl phosphite ozonide (−15 °C, CH_2Cl_2) and the plot of the effective rate constant *vs.* concentration of 1,1-diphenyl-3-diazoacetone (*2*).

Quenching of $^1O_2$ with diazo compounds. In the absence of an acceptor of $^1O_2$

$$I_0 = \frac{\varphi_0\, k_0\, \varphi_2\, [(PhO)_3PO_3]}{k_2},$$

in the presence of A

$$I_A = \frac{\varphi_0\, k_0\, \varphi_2\, [(PhO)_3PO_3]}{k_2 + k_3[A]},$$

hence,

$$I_0/I_A = 1 + k_3/k_2 \cdot [A].$$

Since $1/k_2 = \tau$ (τ is the lifetime of $^1O_2$ in a given solvent), then

$$I_0/I_A = 1 + k_3\, \tau[A], \quad (3)$$

where k_3 is the sum of the rate constants of chemical and physical quenching.

Equation (3) is known as the Stern—Volmer equation. From the dependence of I_0/I_A on [A], one can determine the $k_3\tau$ product or k_3 and τ separately (if τ or k_3, respectively, is known). The applicability of Eq. (3) to the $(PhO)_3PO_3$—solvent—A system is illustrated by the examples given in Fig. 1 and in Table 1.

The overall rate constants decrease as the ionization potential of the $C{=}N_2$ π-bond, IP_1, increases (see Table 1). Analysis of the results shows that the log $[k_3/(k_{diff} - k_3)]$ value ($k_{diff} = 1.34 \cdot 10^{10}$ L mol^{-1} s^{-1} is the diffusion rate constant calculated from the modified Debye equation[13]) depends linearly on the ionization potential of the quenching agent with the correlation coefficient $r = 0.938$ (if the data for compounds **1**, **6**, **10**, and **11** are excluded, $r = 0.989$) (Fig. 3). This dependence holds in the case when electron transfer is the rate-determining process.[14]

$$A + {}^1O_2 \underset{k_{-1}}{\overset{k_{diff}}{\rightleftharpoons}} [A \ldots {}^1O_2] \xrightarrow{k_3} [A^{+\cdot} + O_2^{-\cdot}] \longrightarrow \ldots$$

The linear plot of k_3 *vs.* IP_1 (see Table 1) implies that good overlap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the singlet oxygen (Fig. 4) is one of the main factors favoring this reaction.

The separate determination of the rate constants of chemical and physical quenching of $^1O_2$ was carried out for the reaction of $^1O_2$ with 9-diazofluorene. In conformity with the kinetic scheme, the stoichiometry of the consumption of the ozonide and the diazo com-

Table 1. Rate constants of the reaction of $^1O_2$ with diazo compounds at −15 °C in CH_2Cl_2

Compound	$k_3\tau$ /L mol^{-1}	k_3 ^{a} /L mol^{-1} s^{-1}	IP_1/eV
1	$(7.0\pm2.30)\cdot10^3$	$7.0\cdot10^7$	7.18
2	$(4.41\pm0.33)\cdot10^4$	$4.41\cdot10^8$ $8.30\cdot10^8$ ^{b} $6.00\cdot10^8$ ^{c}	7.24
3	$(1.62\pm0.11)\cdot10^4$	$1.62\cdot10^8$	7.38
4	$(3.68\pm1.00)\cdot10^4$	$3.68\cdot10^8$	7.41
5	$(4.69\pm1.25)\cdot10^3$	$4.69\cdot10^7$ $5.10\cdot10^7$	7.67
6	$(3.44\pm1.50)\cdot10^4$	$3.44\cdot10^8$	7.87
7	$(6.03\pm1.00)\cdot10^4$	$6.03\cdot10^8$	
8	$(5.12\pm0.46)\cdot10^2$	$5.12\cdot10^6$	8.01
9	10.84 ± 2.93	$10.84\cdot10^4$	8.60
10	2.31 ± 0.12	$2.31\cdot10^4$	8.67
11	1.20 ± 0.20	$1.20\cdot10^4$	8.88
12	7.46 ± 0.57	$7.46\cdot10^4$	8.88
13	4.00 ± 0.14	$4.00\cdot10^4$	9.14
14	2.68 ± 0.56	$7.68\cdot10^4$	9.22

[a] In the calculation of k_3, k_2 was assumed to be $1\cdot10^{-4}$ s^{-1} (*cf.* Ref. 12). [b] Measured by the method of competing reactions[2] in CH_2Cl_2 at 25 °C. [c] Measured by flash photolysis[3] in CH_2Cl_2 at 27 °C.

pound obeys the following equation:

$$\frac{[A]_0-[A]_\infty}{[(PhO)_3PO_3]_0}=\varphi_0\varphi_3-\frac{k_2}{k_3}\cdot\frac{\ln([A]_0/[A]_\infty)}{[(PhO)_3PO_3]_0} \qquad (4)$$

Here, $[A]_0$ and $[A]_\infty$ are the concentrations of 9-diazofluorene at the beginning and at the end of the experiment, respectively.

Using $\varphi_0 = 1$ (see Ref. 7) calculated from the I_0/I_A *vs.* $[A]_0$ plot (see Fig. 1), the $k_3/k_2 = (4.69\pm1.25)\cdot10^3$ L mol^{-1} ratio, and the data of Table 2, we obtained $\varphi_3 = 0.14\pm0.3$. Thus, the rate constants of the chemical and physical quenching are $6.56\cdot10^6$ and $4.03\cdot10^7$ L mol^{-1} s^{-1}, respectively.

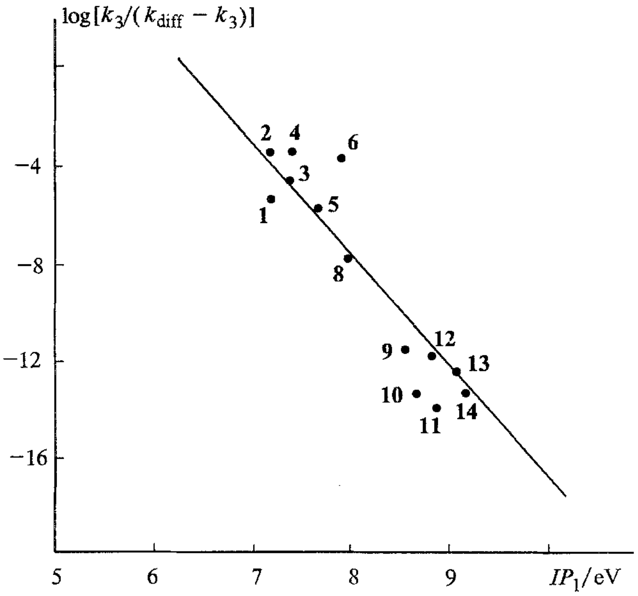


Fig. 3. The plot of the $\log[k_3/(k_{diff}-k_3)]$ parameter *vs.* IP_1. Numbering of the points corresponds to the numbers of compounds.

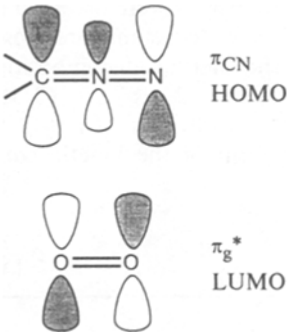


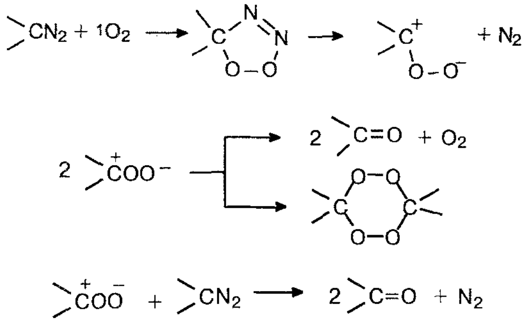
Fig. 4. Interaction of the orbitals in the reaction of $^1O_2$ with diazo compounds.

The oxidation of 9-diazofluorene affords fluorenone. At $[(PhO)_3PO_3]_0 : [A]_0 \approx 10 : 1$, its yield is quantita-

Table 2. The stoichiometry of the consumption of 9-diazofluorene and triphenyl phosphite ozonide (−15 °C, CH_2Cl_2)

$[A]_0\cdot10^4$ /mol L^{-1}	$[A]\cdot10^4$ /mol L^{-1}	$[(PhO)_3PO_3]_0\cdot10^3$ /mol L^{-1}	$\frac{[A]_0-[A]_\infty}{[(PhO)_3PO_3]_0}\cdot10^2$	$\frac{\ln([A]_0/[A]_\infty)}{[(PhO)_3PO_3]_0}$/L mol^{-1}
16.29	5.63	8.27	12.89	128.42
16.10	4.20	9.01	13.20	149.17
7.98	2.17	5.12	11.35	253.91
6.92	0.83	6.11	9.97	347.14

tive. Fluorenone is apparently formed according to the following scheme:[2,3]



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