procedure has been adopted for compounds **2b** (300 mg, 4.5×10^{-3} M) and **2c** (300 mg, 6.3×10^{-3} M). The products and the yields from chromatographic separation are gathered in Table I.

Flash Photolysis Experiments. The laser flash photolysis studies were carried out by using the third (355 nm) and the fourth (266 nm) harmonics of a Q-switched Nd-YAG laser (Model HY 200 JK Lasers Ltd. Lumonics). The detection system consisted of a laser kinetic spectrometer (Model K 347 Applied Photophysics) and an oscilloscope (Tektronix Model 2467 connected to a C 1001 video camera). The trace was registered through an IBM PC/AT.

In the nanosecond experiments, solutions of the heteropentalenes **2** of ca. 5×10^{-5} M in the appropriate solvent (corresponding to an absorbance of ca. 0.4 at the excitation wavelength) were excited by a single shot using the third harmonic (355 nm) of the Nd-YAG laser (the duration and energy of the pulse were approximately 8 ns and 30 mJ, respectively) and analyzed at 370 nm through a Schott glass filter WC295 for compounds **2**, or at the convenient wavelength for the nitrenes and ketone triplets (see text). The optical beam had a path length of 1 cm in the cell and was at a right angle to the excitation pulse.

Solutions of the azides **1** in the appropriate solvent ca. 5×10^{-5} M were excited as described above by using the fourth harmonic (266 nm, 20 mJ pulse^{-1}) and analyzed at 370 nm through a Schott glass filter WG 345. The sample solution was replaced after each shot.

Conventional flash photolysis was carried out by means of an Applied Photophysic K-20 apparatus, using solutions ca. 10^{-5} M of the substrates **1** or **2** in the appropriate solvent in cylindrical tubes, analyzing at 370 nm through the above-mentioned filters. The optical path was 10 cm; the sample solution was replaced after each shot. The kinetic constants for the decay of the transients were obtained manually from oscilloscope traces.

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Registry No. 1a, 78564-50-8; **1b**, 60418-40-8; **1c**, 60418-63-5; **2a**, 60418-46-4; **2b**, 60418-48-6; **2c**, 1738-57-4; **3a**, 78564-51-9; **3b**, 60418-49-7; **4a**, 60418-47-5; **4b**, 60450-52-4; **4c**, 54705-91-8; **5a**, 134817-12-2; **5b**, 134817-13-3; **6a**, 78564-52-0; **6b**, 134817-11-1; **6c**, 1738-59-6; **7c**, 134817-14-4; **10**, 134817-15-5; imidogen, 13774-92-0; benzophenone, 119-61-9; dipropylamine, 142-84-7; acetophenone, 98-86-2; 2-(3,5-dimethylpyrazolyl)phenylnitrene, 78564-49-5.

$O_2^{\bullet -}$ Addition to Ketomalonate Leads to Decarboxylation: A Chain Reaction in Oxygenated Aqueous Solution

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Abstract: Superoxide radical anion, $O_2^{\bullet -}$, was generated radiolytically in oxygenated aqueous formate solutions. In its reaction with ketomalonate ion, oxalic monoperacid and carbon dioxide are formed via a chain reaction. The chain length increases linearly with (dose rate)$^{-1/2}$, i.e. (rate of $O_2^{\bullet -}$ generation)$^{-1/2}$, as well as ketomalonate concentration. Typically, at a dose rate of 0.055 Gy s^{-1} and a ketomalonate concentration of 8×10^{-3} mol dm^{-3} at pH 10 (formate concentration 0.1 mol dm^{-3}), $G(CO_2) = 150 \times 10^{-7}$ mol J^{-1} is found. It is suggested that the propagation steps of this unexpected chain reaction are addition of $O_2^{\bullet -}$ to the keto group of the ketomalonate ion, followed by fragmentation of this adduct into oxalic monoperacid and $CO_2^{\bullet -}$, the latter reducing O_2 and so regenerating $O_2^{\bullet -}$. A propagation rate constant of about 150 dm^3 mol^{-1} s^{-1} has been estimated.

Introduction

The reactions of the superoxide radical anion, $O_2^{\bullet -}$, are attracting increasing attention since they are believed to be implicated in biological cell damage inflicted under normal metabolic conditions or by ionizing radiation.[1,2] In aqueous solutions, $O_2^{\bullet -}$ readily undergoes electron-transfer reactions; otherwise, however, it is quite inert compared to other free radicals (for a review see ref 3), especially with respect to hydrogen abstraction, as the $H-O_2^-$ bond dissociation energy is below 70 kcal mol^{-1} (gas phase[4-6]). Where such a reaction *is* observed (e.g., with *n*-propylgallate), it is believed to be due to an addition reaction, followed by HO_2^- (H_2O_2) elimination.[7] $O_2^{\bullet -}$ is also known (so far only in *nonaqueous solvents*) to act as a nucleophile (for a review see ref 3), leading, e.g., to ester cleavage under alkoxide expulsion and formation of a peroxyacyl radical.[8] In α-keto- and α-hydroxyketones and -esters, $O_2^{\bullet -}$ can bring about oxidative C–C bond cleavage,[9,10] again in nonaqueous solvents.

A well-known reaction *in aqueous solution* leading to $HO_2^{\bullet}/O_2^{\bullet -}$ is its elimination from α-hydroxyalkylperoxyl radicals (reactions 1–3).[11,12] This process plays a major role in the peroxyl radical chemistry of aqueous solutions since many peroxyl radicals which carry an H atom but not an OH group in the α-position eventually are still converted into α-hydroxyalkylperoxyl radicals.[2]

$$R_2C(OH)O_2^{\bullet} \rightarrow R_2C{=}O + HO_2^{\bullet} \quad (1)$$

$$R_2C(OH)O_2^{\bullet} + OH^- \rightarrow R_2C(O^-)O_2^{\bullet} + H_2O \quad (2)$$

$$R_2C(O^-)O_2^{\bullet} \rightarrow R_2C{=}O + O_2^{\bullet -} \quad (3)$$

In the course of a radiation chemical study of hydroxymalonic acid where the $O_2^{\bullet -}$ elimination sequence (1–3) is also operative,[13]

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we have made the interesting observation that the resulting ketomalonic acid is capable of undergoing an oxidative *chain reaction* with $O_2^{\bullet -}$. This has determined us to investigate the ketomalonic acid/$O_2^{\bullet -}$ system independently in more detail.

Experimental Section

N_2O/O_2 (4:1 v/v) saturated aqueous solutions of formic acid (Merck p.a., 10^{-2} and 10^{-1} mol dm^{-3}) containing various amounts ((1-7.5) × 10^{-3} mol dm^{-3}) of ketomalonic acid (monohydrate, 99%, Janssen) were irradiated at 20 °C with ^{60}Co γ rays at dose rates of 0.018-0.47 Gy s^{-1}. The pH of the solutions was adjusted with sodium hydroxide.

For the determination of carbon dioxide, the irradiated solutions were acidified with concentrated sulfuric acid to pH 1 through a serum cap and the CO_2 with a stream of argon flushed into an evacuated flask. An aliquot was determined by GC on a 2m Porapak column (FID, room temperature, H_2 as carrier gas) after on-line catalytic reduction to methane. The unirradiated blanks were treated in the same way.

In analogy to oxalic diperacid,[14] solutions of oxalic monoperacid were prepared by reacting an excess of hydrogen peroxide (extracted from 30% aqueous hydrogen peroxide with diethyl ether) with oxalyl chloride in pyridine. In contrast to oxalic acid, oxalic monoperacid does not form a precipitate with calcium ions. When treated with triphenylphosphine in ether solution, oxalic peracid is reduced to oxalic acid. Upon use of Allen's reagent,[15] oxalic monoperacid, which is insensitive to catalase treatment, reacts rapidly with KI ($t_{1/2} < 10$ s). Oxalic monoperacid can be separated from formic acid (2 min) and ketomalonic acid (25 min) by ion chromatography (Dionex 2010 i, Dionex ion pac columns MPIC-NG1 + HPIC-AS4 with suppressor AFS-1, eluent 1.4 × 10^{-3} mol dm^{-3} $NaHCO_3$ and 1.1 × 10^{-3} mol dm^{-3} Na_2CO_3, flow rate 1.5 × 10^{-3} dm^3 min^{-1}). The retention time is 12 min, identical with that of oxalic acid. However, in contrast to oxalic acid which is completely removed by treatment of the sample with calcium ions, the HPIC peak at 12 min remains unchanged in an irradiated solution when calcium has been added, indicating that this peak is *not* due to oxalic acid. A sample collected by repetitive HPIC and subsequent concentration by rotary evaporation with irradiated material showed the same behavior as exhibited by the synthesized material. For quantification of the HPIC signals the same response factor as that of oxalic acid was used. The correctness of this procedure was confirmed by the iodometric titration of an isolated sample.

Oxygenated solutions of oxidizable substrates may under certain conditions undergo autoxidation. In order to verify the absence, in the system under study, of such a process, a 10^{-3} M ketomalonate solution brought to pH 14 was aerated ($[O_2] = 2.6 \times 10^{-4}$ mol dm^{-3}). The oxygen concentration was then monitored with a Clark electrode and after 1 h found unchanged within experimental error (by less than 3 × 10^{-7} mol dm^{-3}).

In order to determine the proportion of the carbonyl form of the ketomalonate ion, proton-decoupled ^{13}C NMR spectra of the substrate (0.25 mol dm^{-3}) in D_2O were recorded on a Bruker AM 400 instrument (at 100.6 MHz with an internal deuterium lock) operating in the Fourier transform mode. An average of 1000 Scans with a pulse frequency of 2 s^{-1} and a pulse angle of 30° was used to record a spectrum. Sodium 3-(trimethylsilyl)propionate-d_4 was used as an internal standard. The ^{13}C chemical shifts in ppm downfield from that of the internal standard are δ 95 (C-2, hydrate form), 172 ($-CO_2^-$ of keto form), 178 ($-CO_2^-$ of hydrate form), and 196 (C-2, carbonyl form). At pD 1 in the temperature range 20-60 °C, only the hydrate signals could be observed. However, at pD 7.4 and 9, the carbonyl signals (≈10% at 20 °C, ≈60% at 70 °C) could be observed alongside the hydrate signals.

Since the relative importance of OH radical attack at the ketomalonate ion in the formate-containing system had to be determined, pulse radiolysis was performed on formate-free N_2O-saturated ketomalonate solutions, with a 2.8 MeV Van de Graaff electron generator delivering 0.4-1 μs electron pulses of 2-20 Gy. The setup with the optical detection techniques as well as the data processing procedures have been described.[16,17]

Results and Discussion

Generation of Superoxide Radical Anion. Aqueous superoxide radical anion is most conveniently generated radiolytically from formate ion in N_2O/O_2 (4:1 v/v) saturated solutions (reactions 4-9).[2] Under these conditions the radiation chemical yields are $G(^\bullet OH) = 6 \times 10^{-7}$ mol J^{-1} and $G(H^\bullet) = 0.6 \times 10^{-7}$ mol J^{-1}, i.e., $O_2^{\bullet -}$ is formed with a yield of $G(O_2^{\bullet -}) = 6.6 \times 10^{-7}$ mol J^{-1}. In the absence of a reactive substrate, $O_2^{\bullet -}$ generated in this system merely undergoes dismutation with its conjugated acid $HO_2^\bullet$ yielding hydrogen peroxide and oxygen (reaction 10). The only other relevant product is carbon dioxide.

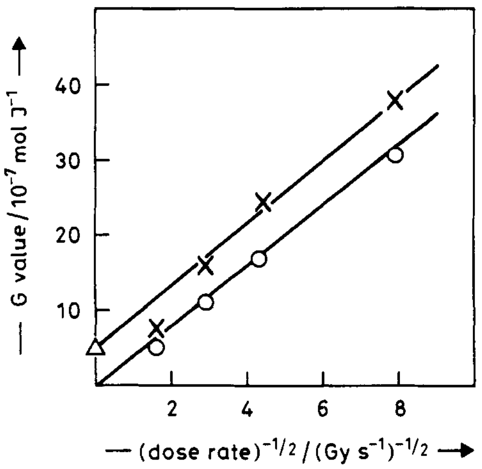

Figure 1. *G* values (in units of 10^{-7} mol J^{-1}) of carbon dioxide (×) and oxalic monoperacid (○) as a function of (dose rate)$^{-1/2}$ in the γ-radiolysis of N_2O/O_2 (4:1) saturated aqueous solutions at pH 10 containing 0.01 mol dm^{-3} formate ions and 10^{-3} mol dm^{-3} ketomalonate ions at 20 °C. The value for carbon dioxide in the absence of ketomalonic acid (△) was taken for the value at infinitely high dose rate (absence of chain reaction).

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} {}^\bullet OH,\ e_{aq}^-,\ H^\bullet,\ H^+,\ H_2O_2,\ H_2 \qquad (4)$$

$$e_{aq}^- + H_2O \rightarrow {}^\bullet OH + N_2 + OH^- \qquad (5)$$

$$^\bullet OH + HCO_2^- \rightarrow H_2O + CO_2^{\bullet -} \qquad (6)$$

$$H^\bullet + HCO_2^- \rightarrow H_2 + CO_2^{\bullet -} \qquad (7)$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet\ (pK_a = 4.8)^{18} \qquad (8)$$

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \qquad (9)$$

$$O_2^{\bullet -} + HO_2^\bullet \rightarrow O_2 + HO_2^- \qquad (10)$$

In the γ-radiolysis of an N_2O/O_2 (4:1 v/v) saturated solution of 10^{-2} mol dm^{-3} formate containing 10^{-3} mol dm^{-3} ketomalonate [pK_a(ketomalonic acid) = 1.6 and 3.9, as determined by titration], the OH radicals undergo reaction practically exclusively with the formate. This is readily verified from the concentrations of the solutes and the rate constants of their reactions with the water radicals. Reported rate constants (dm^3 mol^{-1} s^{-1}) are $k_5 = 9.1 \times 10^9$,[19] $k_6 = 3.2 \times 10^9$,[19] $k_7 = 2.1 \times 10^8$,[19] $k_8 = 2.1 \times 10^9$,[19] $k_4 = 2.4 \times 10^9$,[20] and $k_{10} = 9.7 \times 10^7$.[18] In the absence of data on the rate constants for the reaction of OH with ketomalonic acid/ketomalonate, we have now determined them pulse radiolytically for the anions, with SCN^- as the competitor, $k(^\bullet OH + SCN^-) = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.[19] At pH 3, $k(^\bullet$OH + ketomalonic acid monoanion) = 5.7 × 10^7 dm^3 mol^{-1} s^{-1}, and at pH 9, $k(^\bullet$OH + ketomalonic acid dianion) = 1.0 × 10^8 dm^3 mol^{-1} s^{-1}.

Evidence for the Existence of a Chain Reaction. In the absence of ketomalonate, carbon dioxide is formed with a *G* value of about 6.6 × 10^{-7} mol J^{-1}. In Figure 1, this is represented by the triangle. In the presence of ketomalonate the yields are considerably higher

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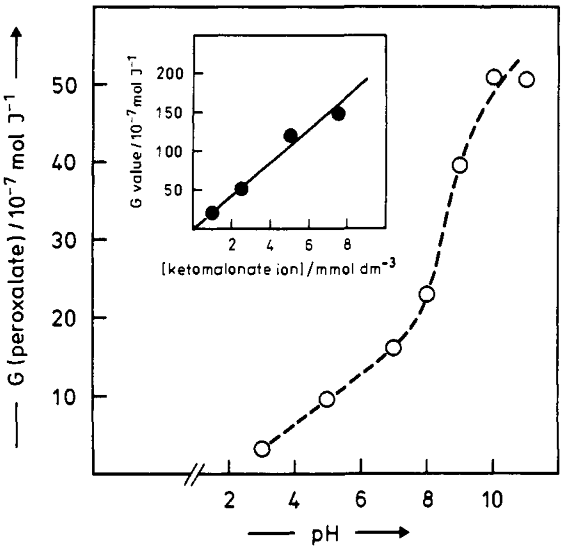


Figure 2. *G* value (in units of 10^{-7} mol J^{-1}) of oxalic monoperacid as a function of pH in the γ-radiolysis of N_2O/O_2 (4:1) saturated solutions of formate ions (0.01 mol dm^{-3}) containing 2.5×10^{-3} mol dm^{-3} ketomalonic acid at 20 °C and a dose rate of 5.5×10^{-2} Gy s^{-1}. Inset: *G* value of oxalic monoperacid as a function of ketomalonate concentration at pH 10 and 0.1 mol dm^{-3} formate.

(Figure 1; inset Figure 2). Under our conditions, $G(CO_2)$ values as high as 150×10^{-7} mol J^{-1} are observed, a clear indication for the existence of a chain reaction.

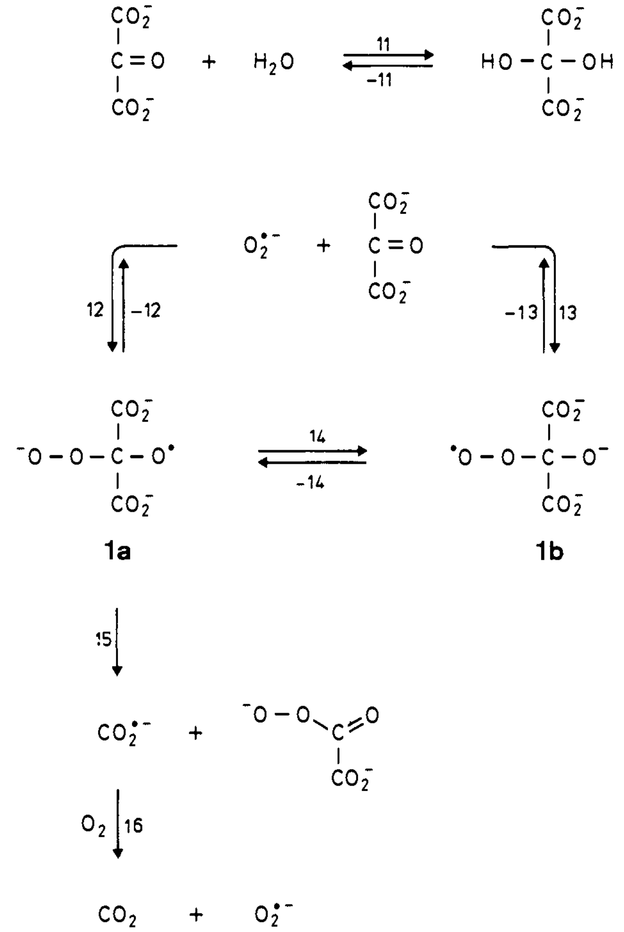
In Figure 1, the radiation chemical yield of carbon dioxide is plotted as a function of the inverse of the square root of the dose rate ($r^{-1/2}$). Again, the linear relationship is typical for a chain reaction. The complementary two-carbon product has been identified as oxalic monoperacid. Its yield matches satisfactorily that of carbon dioxide (cf. Figure 1), account being taken of the oxidation of the formate ion in reactions 6, 7, and 9. This contribution is represented by the intercept.

Also another condition of a chain reaction is met: the dependence of the chain length from the concentration of the relevant substrate. That this is indeed the case is shown in the inset of Figure 2 where it can be seen that at a given dose rate the *G* value of the chain product increases linearly with increasing ketomalonate concentration.

Mechanistic Considerations. We have seen that ketomalonate is not attacked by any of the water radicals. If $CO_2^{\bullet -}$ reacted with the ketomalonate, the latter would be reduced to the ketyl radical. But this has been shown[13] to react readily with oxygen, followed by $O_2^{\bullet -}$ elimination and ketomalonate restitution ($t_{1/2} < 8$ μs). This means that $O_2^{\bullet -}$ is formed with a *G* value equal to $G(^{\bullet}OH + H^{\bullet})$, just as in the oxygenated formate system without additive. Another potentially reactive component is O_2 which is of course always present in our experiments, and the possibility of an autoxidative process must be kept in mind. However, the blanks never contained any CO_2 and oxalic monoperacid. Not even at pH 14, beyond our experimental pH range (see Figure 2), did hydroxide ion exert a catalytic effect (as a referee suggested it might). As evidenced by the oxygen-uptake measurement, *no* autoxidation takes place. In this context, it must be emphasized that side effects of the generation of $O_2^{\bullet -}$ in organic solvents when KO_2 is used as the source are not expected (and not observed) when $O_2^{\bullet -}$ is generated radiolytically in aqueous solutions.

Thus we must conclude that the chain reaction leading to oxalic monoperacid and CO_2 is $O_2^{\bullet -}$-initiated and is best explained on the basis of a sequence of reactions as summarized in Scheme I. Addition of $O_2^{\bullet -}$ to ketomalonic acid leads to radical **1a** and/or **1b**, i.e., free-radical addition (reaction 12; there are examples for the addition of acyl[21] or alkyl[22] radicals to the carbonyl function)

Scheme I



and/or nucleophilic addition (reaction 13) may take place. Bearing in mind the weak radical nature of $O_2^{\bullet -}$ as well as its weak nucleophilicity in water, we do not favor one over the other. In any case, both species **1a** and **1b** may interconvert by intramolecular solvent-induced electron-transfer reactions 14/−14; rate constants for certain other interconversion processes are substantial.[23] Besides equilibrium 14 one might also consider an electron transfer involving the carboxylate group of **1b**. The resulting radical is expected to readily decarboxylate, and subsequent reactions could lead to the observed products. This mechanistic alternative has not been included in the scheme as we have shown previously that the peroxyl radical derived from the acetate ion does not undergo a unimolecular reaction of this kind.[24]

The fragmentation of **1a** (cf. the elimination of methyl from *tert*-butoxyl radical where $t_{1/2}$ in aqueous solutions is only ca. 1 μs[25]) with loss of $CO_2^{\bullet -}$ gives rise to the monoperoxyoxalic acid (reaction 15).

It is suggested that in reactions 12 and 13 $O_2^{\bullet -}$ reacts with the carbonyl form of the ketomalonate dianion, which is in equilibrium with its hydrate (reactions 11/−11). The $CO_2^{\bullet -}$ radical formed in reaction 16 reacts with oxygen (reaction 9) to give carbon dioxide and the superoxide radical. The bimolecular dismutation of the superoxide radical with its conjugated acid (reaction 10)[18] is the chain terminating step.

The hydration constant of ketomalonic acid has been reported to be 10^2 ([hydrate form]/[carbonyl form]) at 25 °C in a 0.1 mol dm^{-3} solution (pH 1.7).[26] We have determined its presence by

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^{13}C NMR spectroscopy. The data indicate that for the protonated acid the hydrate form is strongly predominant, with very little free carbonyl to be observed in the equilibrium. For the dianion, however, the carbonyl form is present to ca. 10% at 20 °C, its proportion increasing linearly with temperature. This behavior resembles that observed in carbohydrates (cf. ref 27).

The data shown in Figures 1 and 2 suggest an attempt to estimate the lower limit for the rate constant of $O_2^{\bullet-}$ addition; if this reaction is considered to be the rate-limiting step of the propagating sequence, its rate constant k_{addition} can be extracted. In the steady-state approximation from $v_{\text{initiation}} = v_{\text{termination}}$ we obtain $[O_2^{\bullet-}]_{\text{steady state}}$. Moreover, $v_{\text{propagation}} = k_{\text{addition}} \cdot [O_2^{\bullet-}]_{\text{steady state}}[-CO-]$, where –CO– signifies ketomalonate carbonyl form.

The present situation is described by equation 17 (*r*, dose rate). There are two sets of experiments which allow the calculation of k_{addition}: the dose rate dependence in Figure 1 and the ketomalonate dependence shown in the inset of Figure 2. The former data set yields $k_{\text{addition}} = 120\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$, and from the latter $k_{\text{addition}} = 150\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ is calculated. Considering that two independent data sets are used the agreement is quite satisfactory.

$$G(\text{peroxalate}) = \{G(O_2^{\bullet-})\}^{1/2} \left(\frac{k_{\text{addition}}}{(k_{10})^{1/2}} \right) \frac{[-CO-]}{r^{1/2}} \quad (17)$$

The lowering of the pH to 3 brings about the protonation of the ketomalonate dianion, i.e., a lower contribution of the substrate in its reactive form (reaction 11) as well as an increase in the rate of chain termination through protonation of the superoxide radical anion.[28] Accordingly at pH 3 (Figure 2) the chain reaction is very ineffective. The fact that it goes on at all is in line with the assumption that $HO_2^{\bullet-}$ which predominates at this pH exhibits some reactivity with respect to radical addition to the ketomalonic acid. At higher pH the intrinsic lifetime of $O_2^{\bullet-}$ is longer since it can only terminate according to reaction 10. Thus the chain reaction is more effective at higher pH.

The behavior of the chain reaction following a change in the temperature is noteworthy. Even though the equilibrium contribution of the carbonyl form increases from 10% at 20 °C to ≈60% at 70 °C according to our ^{13}C NMR data, the monoperoxyoxalic acid yield of a formate solution containing ketomalonic acid γ-irradiated at pH 10 remains practically unchanged when the temperature of the reaction system is raised from 20 to 70 °C. One reason might be that the increase in the proportion of the carbonyl form is offset mainly by the decrease in the ratio $k_{\text{addition}}/k_{\text{reverse}}$ which seems reasonable since the adducts **1a** and **1b** are in this sense analogous to the hydrate.

Final Remarks

Because of the intrinsically long lifetime of $O_2^{\bullet-}$ radicals, the interesting question arises as to whether such addition reactions occur with other systems as well and whether, on top of its well-documented transition-metal-ion-induced damaging properties to biological systems,[2] the type of reaction discovered here can contribute to the deleterious effects of $O_2^{\bullet-}$.

In fact, another chain reaction involving the $O_2^{\bullet-}$ radical has recently been discovered in our laboratory,[29] and work is in progress demonstrating the unexpected versatility of $O_2^{\bullet-}$-induced reactions in aqueous solutions. Again, radiation techniques are the methods of choice in their elucidation.

Registry No. $O_2^{\bullet}$, 11062-77-4; $^{-}OCOCOCOO^{-}$, 4004-36-8; $^{-}OOCO\dot{}COO^{-}$, 135189-92-3.

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Quantum Yields in the Photochemically Induced Radical Chemistry of Acyl Derivatives of Thiohydroxamic Acids

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received April 9, 1991. Revised Manuscript Received May 24, 1991*

Abstract: Acyl derivatives of *N*-hydroxyquinazoline-4-thiones are a novel source of disciplined carbon radicals. Quantum yield determination reveals that photolysis of these compounds initiates radical chains, resulting in quantum yields up to $\Phi = 60$. Comparative studies with acyl derivatives of *N*-hydroxy-2-thiopyridone show that the quinazoline derivatives are more light-sensitive than the thiopyridone compounds. The carbon radicals thus formed from the former can be trapped selectively, without the formation of rearranged products (i.e. without the competition of the radicophilic thiocarbonyl group of the starting material with the radical trap).

Introduction

Radical chemistry has become an important tool in synthetic organic chemistry during the past 10–15 years.[1-10] This is related to the selectivity and mild reaction conditions associated with these reactions. The selectivity most often is a result of the disciplined

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