RADICAL NATURE OF CHEMILUMINESCENCE IN THE PROCESS OF OXIDATION OF ETHYLALUMINUM DIETHOXIDE BY OXYGEN

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The mechanism of oxidation of trialkylaluminum compounds R_3Al by oxygen in solution is described by a scheme that includes a series of consecutive-parallel molecular reactions [1, 2]. Ordinarily, in describing the oxidation of organoaluminum compounds (OACs), radical reaction mechanisms are invoked only to explain the fact of byproduct formation. The formation of radicals by the interaction of OACs with O_2 was also suggested in [3, 4] on the basis of the ability of the OAC/ O_2 system to initiate the polymerization of monomers.

Direct evidence for a free radical mechanism was obtained in [5]; however, this pertained only to the first stage of oxidation of Me_3Al , i.e., to the formation of an organoaluminum peroxide (OAP); this mechanism does not extend to the second stage of the process, in which the OAP that has been formed reacts with the original OAC.

The work reported here represents an attempt to elucidate the role of free radicals in the oxidation of alkoxy derivatives of triethylaluminum (TEA) under conditions of simultaneous and separate occurrence of the stages of formation and consumption of the OAP; the work was further aimed at investigating the mechanism of the chemiluminescence (CL) that accompanies the OAC oxidation process [6, 7]. As an object of investigation we selected ethylaluminum diethoxide, which has only one Al-C bond, the oxidation of which is accompanied by CL.

EXPERIMENTAL

The synthesis, purification, and analysis of the ethylaluminum diethoxide (DO) and the purification of the activator 9,10-dibromoanthracene (DBA) were performed in accordance with [7], that of the galvinoxyl (In') in accordance with [8]. The In' was identified by its ESR and UV spectra. The kinetics of In' consumption were studied spectrophotometrically (E at 423 nm = $24.3 \cdot 10^3$ M⁻¹) in a cuvette (1 cm) sealed with a tight stopper (in a Specord UV-VIS spectrophotometer). The oxygen, air, and argon were purified by means of a PG gas purification apparatus.

The CL was measured in a unit that has been described in [7]. The oxidation of the DO in toluene (with simultaneous recording of CL) was performed by three methods: 1) by bubbling O_2 or air through the solution at a rate such that the measurements were carried out in the kinetic regime; 2) by introducing an aliquot of the DO by means of a syringe into a cuvette containing toluene that was saturated with the oxidizing gas, followed by oxidation by the dissolved O_2 in a volume enclosed by the ground-in cover, this volume not containing any gas phase; 3) by absorption of O_2 from a burette at constant atmospheric pressure after introducing the DO by means of a syringe into the cuvette through the seal plug. The cuvettes were thermostated by circulating water from a thermostat. The OAP concentration was determined by iodometric titration [9].

DISCUSSION OF RESULTS

The intensity of CL in the oxidation of DO is highly dependent on the purity of the original compound. For example, as a result of three redistillations of DO under conditions eliminating any possible contact with vacuum grease, the CL disappears almost completely. However, in the presence of the DBA, rather bright CL is observed ($>3\cdot10^6$ photons/sec·ml). The shape of the CL kinetic curves is the same whether the inadequately purified DO is oxidized or whether the pure product is oxidized in the presence of the DBA; i.e., in both cases, we are dealing with activated CL. The absence of inactivated CL is related to the low luminescence yield from the primary CL emitter that is formed upon oxidation of DO.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1747-1753, August, 1984. Original article submitted May 23, 1983.



Fig. 1. Kinetic curves for oxidation of $(EtO)_2AlEt$ in toluene, by oxygen: 1) O_2 absorption; 2) CL intensity; 3) OAP accumulation. [DBA] = 10^{-4} M, 20° C, $[O_2] = 6 \cdot 10^{-3}$ M (const), solution volume 40 ml.

Oxygen, which is necessary for the generation of CL, interacts with DO to form the corresponding OAP in the first stage of oxidation,

$$(\text{EtO})_2 \text{AlEt} + \text{O}_2 \rightarrow (\text{EtO})_2 \text{AlOOEt}$$
(1)

after which the OAP is consumed in the second stage, giving the trioxide as the principal end product:

$$(EtO)_{2}AlEt + (EtO)_{2}AlOOEt \rightarrow (EtO)_{3}Al$$
(2)

In order to obtain data on the relative rates of reactions (1) and (2), we investigated the kinetics of O_2 absorption and the changes in concentration of the OAP as the DO is oxidized. From the typical kinetic curves (Fig. 1, curves 1 and 2), we can conclude that only 0.6 mole of O_2 is absorbed per mole of DO; i.e., approximately 60% of the DO is consumed in reaction (1) to form the OAP (the OAP is the main product from this reaction [2]). This means that the second stage plays an important role in the kinetics of DO consumption.

The orders of reaction (1) with respect to DO (n = 1) and with respect to O₂ (m = 0) were determined from the slopes of the lines corresponding to the equation $\log W_0 = \log K_1 + n \log$ $[D0] + m \log [0_2]$, with the DO concentration in the first case varied over the interval (0.5-2.0) $\cdot 10^{-1}$ M (with $[0_2] = 6 \cdot 10^{-3}$ M, const), and with the concentration of 0_2 in the second case varied in the interval $(1.2-6.0)\cdot 10^{-3}$ M (with [D0] = 10^{-1} M, const). Here, W_o is the mean initial rate of O₂ absorption, determined from the slope of the initial section of a curve analogous to curve 1 in Fig. 1. The magnitude of the pseudo-first-order rate constant $(k_1 = k_1)$ $W_0/[D0]$) is $k_1 = (2.3 \pm 0.1) \cdot 10^{-4} \text{ sec}^{-1}$. The ratio of the mean rates of reactions (1) and (2), calculated from the consumption of O2 and OAP at the time the maximum content of OAP is reached in the solution (τ_{max}) , is $\overline{W}_1/\overline{W}_2 = (\Delta[O_2]/\tau_{max})/(\Delta[OAP]/\tau_{max}) = 2$, where $\Delta[O_2]$ is the quantity of O₂ absorbed; $\Delta[OAP]$ is the consumption of OAP, given by $[OAP]_{theor} = \Delta[O_2] - [OAP]_{exp}$. The value obtained for the ratio of the mean rates indicates that the second stage of oxidation is the slower of the two. An analogous result was obtained in [10] in a comparison of the rates of two stages of oxidation of the first Al-C bond in $Al(C_6H_{13})_3$. It can be seen that for all of the alkylaluminums, the interaction of the OAP with the original OAC from which the peroxide is obtained is the slower reaction. This conclusion is further supported by the registration of two consecutive maxima in the kinetic dependence of the CL intensity that reflects the process of consumption and accumulation of such highly reactive OAPs as $Et_2A100Et$ and EtA1(00Et). (OEt), which are formed in the oxidation of Et₃Al.

Both stages of oxidation of the DO, which are represented in the form of reactions (1) and (2), reflecting only the overall process of DO oxidation, have mechanisms that are more complex, as evidenced clearly in an investigation of the influence of the concentration of O_2 and added in In[•] on the kinetics of the dark process and the CL in the oxidation of DO.



Fig. 2. Variation of CL intensity with time in the oxidation of $(\text{Et0})_2\text{AlEt} \cdot (10^{-1} \text{ M})$ in toluene with different concentrations of O_2 : 1) oxidation by air, $[O_2] = 1.2 \cdot 10^{-3} \text{ M} (\text{const})$; 2) oxidation by oxygen, $[O_2] = 6 \cdot 10^{-3} \text{ M} (\text{const})$. In both cases, $[\text{DBA}] = 10^{-4} \text{ M}$, solution volume 10 ml, 20°C. Dashed curve reppresents a typical curve registered when the air bubbling is replaced by argon (A), and then argon by air (B).

Fig. 3. Variation of CL intensity with time in the oxidation of toluene solutions of $(\text{EtO})_2\text{AlEt}$ in a closed volume under conditions of oxygen consumption, with following initial concentrations of dioxide, M: 1) 10^{-1} ; 2) $2.5 \cdot 10^{-2}$; 3) $2.0 \cdot 10^{-2}$; 4) $1.5 \cdot 10^{-2}$; 5) 10^{-1} . Curves 1-4 are for oxidation by oxygen, curve 5 for oxidation by air. In all cases, [DBA] = 10^{-4} M, 20°C, solution volume 20 ml.

It was shown that the CL intensity when DO is oxidized by air is proportional to the concentration of OAP formed in the first stage. Therefore, keeping in view that $\overline{W}_1 > \overline{W}_2$, we had expected that in the oxidation of DO by an oxidizing agent that is more powerful than air pure oxygen - the CL intensity would be higher because of the greater yield of the OAP. However, we found that the increase in the concentration of the oxidizing agent led to a decrease in the CL intensity (Fig. 2, curves 1 and 2). The removal of 0_2 from the solution produced an abrupt increase in the CL intensity (see Fig. 2, point A); subsequent reintroduction of air into the solution gave a sharp drop in the CL intensity. It was also found that when the DO oxidation was performed under conditions of a constantly decreasing O2 concentration (Fig. 3, curves 1-4), bright luminescence did not appear immediately after adding the DO, but rather after a certain induction period (τ_{ind}). During the course of τ_{ind} , only weak CL was observed. The induction period τ_{ind} increased up to 5 h or longer as the [D0]/[0₂] ratio was decreased (Fig. 3, curves 1-4); and with identical concentrations of DO, the induction period increased with increasing 0_2 concentration (curves 1 and 5). The results from these experiments indicate that the oxygen in the system is not only a CL generator, but also a CL deactivator, and this is responsible for the induction period that shows up at the start of the process.

The deactivating role of O_2 may be related either to a quenching action with respect to the CL emitter or to inhibition of the reactions responsible for excitation of the CL; another possibility is a combined action of both these factors. The experimental data obtained thus far do not enable us to choose between these possible reasons for the deactivating effect of the O_2 . In any case, in the role of a quenching agent, the O_2 can act only with respect to the primary emitter of CL, since the secondary emitter, DBA (radiation of which was also registered in the CL) is not quenched by oxygen [11]. The products of the reaction DO + O_2 likewise do not quench the luminescence of the DBA. We established this fact on the basis of the lack of any change in the intensity of DBA photoluminescence when O_2 is introduced into a deaerated solution of DBA containing DO. Thus, with increasing concentration of the oxidizer (O_2), the CL intensity decreases, whereas the rate of the first stage of oxidation of the DO remains unchanged, as does the OAP yield.

The formation of free radicals in this system was detected as a result of oxidation of DO in the presence of In'. As can be seen from Fig. 4 (curves 1 and 2), when In' is added to a



Fig. 4. Effects of inhibitor on oxidation of $(EtO)_2AlEt (10^{-1} \text{ M})$ in toluene: 1) CL intensity; 2) quantity of O_2 absorbed. τ_1 is the moment of adding In'; τ_2 is the end of the induction period. [DBA] = 10^{-4} M, 20°, solution volume , 10 ml, [In'] = $2 \cdot 10^{-5}$ M.

Fig. 5. Changes in kinetics of O_2 absorption (1'-3') and CL intensity (1-3) upon addition of different quantity of inhibitor before the start of oxidation of $(EtO)_2AIEt: 1, 1')$ without In'; 2, 2') $[In'] = 2.1 \cdot 10^{-6}$ M; 3, 3') $[In'] = 5.3 \cdot 10^{-6}$ M; for these curves, $[DO] = 10^{-1}$ M. Curves 4-6 represent kinetics of inhibitor consumption in toluene solution: 4) $5.3 \cdot 10^{-5}$ M In' without O_2 ; 5) $4.5 \cdot 10^{-5}$ M In' + 10^{-1} M (EtO)_2AIEt; 6) $1.7 \cdot 10^{-5}$ M In' + 10^{-1} M (EtO)_2AIEt + $1.2 \cdot 10^{-3}$ M O_2 .

solution of D0 that is being oxidized, the absorption of O_2 and the increase in CL intensity are completely cut off. After the passage of an induction period, the quantity of absorbed O_2 and the CL intensity again increase. If the In' is added before starting the feed of O_2 into the solution, the appearance of the CL and the absorption of the O_2 likewise take place after an induction period (τ_{ind}). A reduction of the quantity of added In' leads to a decrease in τ_{ind} for the absorption of O_2 and for the appearance of CL (Fig. 5, curves 1-3).

It is interesting to note the difference between the results of observations from experiments with the addition of In in the oxidation of DO in our work and in the oxidation of Me₃Al in [5]. The addition of In' to Me₃Al brought about instantaneous coloration of the solution, which then, over the course of 30 sec, changed in color to a pale yellow, and then to deeper tones upon oxidation. It was concluded in [5] that the inhibitor for the oxidation of Me_3Al is a product from the interaction of In' with Me₃Al. We observed that when In' was added, either at the beginning or in the course of the DO oxidation process, there was only a slow decolorization of the original brownish yellow color of the In'. These observations, along with the absence of any changes in the position of the absorption band of the In $(\lambda$ 420 nm) and the extremely slow decrease in its intensity, in comparison with the instantaneous stoppage of the DO oxidation when the In was added, led us to the conclusion that the inhibitor of the DO oxidation product is the In' itself, not a product of its interaction with the DO. Spectrophotometric measurements of the kinetics of In * consumption (Fig. 5, curves 4-6)_showed that this process is accomplished very slowly in a deaerated toluene solution; here, W, In is the maximum slope of the plot of $([\text{In}']_0 - [\text{In}]_7)$ vs $\tau = 4.5 \cdot 10^{-10} \text{ M}^{-1} \cdot \text{sec}^{-1}$. Upon addition of the DO, the process is accelerated $(W_2^{\text{In}'} = 6 \cdot 10^{-9} \text{ M}^{-1} \cdot \text{sec}^{-1})$; and when both DO and O₂ are present, the acceleration is still greater $(W_3^{\text{In}'} = 3 \cdot 10^{-8} \text{ M}^{-1} \cdot \text{sec}^{-1})$. The nonlinear relationship between Tind and [In'] in this system indicates the absence of any simple relationship $(W_o = f[In']/\tau_{ind})$ between the rate of initiation (W_o) and the concentration of inhibitor, of the sort that was observed in the inhibition of oxidation of $(CH_3)_2Cd$ and $(CH_3)_2Zn$ [12].

Thus, from the experiments on the influence of galvinoxyl on the kinetics of DO oxidation by oxygen, we can conclude that the first stage of the process proceeds entirely through a free radical mechanism.

With the aim of elucidating the nature of the second stage of DO oxidation, the galvinoxyl was added after removing oxygen by purging the solution with argon (Fig. 6, curve 3), after which there remained in the solution the OAP and the DO, but the first stage was stopped because of the absence of O_2 . Under these conditions, we did not observe any appreciable retardation of the process of OAP consumption (the corresponding kinetic curves are not shown



Fig. 6. Influence of inhibitor on kinetics of CL in the interaction of $(EtO)_2AlEt$ with atmospheric oxygen (1, 2) and $(EtO)_2AlEt$ with $(EtO)_2AlOOEt$ (3). [DBA] = 10^{-4} M, 20° C; $[(EtO)_2AlEt] = 10^{-1}$ M (1, 3) or $3 \cdot 10^{-1}$ M (2); $[In^{*}]_{0} = 10^{-5}$ M. The arrows indicate the moment of adding In^{*}; the dashed lines indicate the changes in intensity of CL in parallel experiments. A is the moment of initial removal of oxygen from the solution by argon.

here), and the intensity of CL increased by a factor of more than 2. This means that the consumption of the OAP is accomplished mainly without the participation of free radicals. The same can be said about the sources of CL generation under conditions of stoppage of the first stage of the oxidation. Since such a stoppage was accompanied by a simultaneous drop in the CL intensity, it would seem that we should conclude that CL is excited specifically in the first stage of oxidation. However, in this case, the removal of O_2 from the solution would lead to disappearance of the CL, and this did not occur. Probably, even though the CL is not excited in the first stage of oxidation, this stage does generate products that subsequently enter into reaction with the formation of excited states. One of such products is the OAP, since the intensity of CL is proportional to the OAP concentration. This is not, however, the sole source of the CL, since when the first stage is completely stopped by the addition of the galvinoxyl, the generation of the OAP is ended, and its concentration in the solution decreases very slowly in comparison with the instantaneous drop in CL intensity (Fig. 4, curve 1). Therefore, the second product in the first and second stages, participating in the CL generation, is a free radical.

Thus, the complete set of results on the influence of added inhibitor on the kinetics of CL in the oxidation of DO indicates the presence of two sources of CL generation: radical and molecular reactions.

On the basis of the experimental facts obtained in this work, along with literature data on an investigation of the mechanism of oxidation of heteroorganic compounds [1], we can represent the first stage in the DO oxidation by the following scheme, where the notation (>A1') denotes R' or >A1':

$$(RO)_2 AIR + O_2 \rightarrow R^{\bullet} (>AI^{\bullet}) \qquad \text{chain initiation} \tag{0}$$

$$\mathbf{R}^{\bullet}(\mathbf{A}\mathbf{I}^{\bullet}) + \mathbf{O}_{2} \to \mathbf{R}^{\bullet}(\mathbf{A}\mathbf{I}^{\bullet})\mathbf{O}_{2}^{\bullet}$$
(1)

$$RO_2' + >AIR \rightarrow >AIOOR + R'$$
 (2)

$$>AlO_2$$
 + $>AlR \rightarrow >AlOOAl < + R$ (3)

Under the conditions of the developing process, another initiating reaction may be the process of thermal decomposition of the OAP. Homolytic substitution at the Al atom in accordance with reaction (3) is less probable than according to (2), since the possibility of forming a peroxide of the type of >AlOOAl < has not thus far been confirmed experimentally.

The stoppage of the first stage by the inhibitor is related to the reaction

$$R (>Al)O_2^{\bullet} + In^{\bullet} \rightarrow R (>Al)O_2In$$
(4)

Under conditions of independence of the rate of DO oxidation from the O_2 concentration, all of the radicals not containing oxygen are converted to peroxides in accordance with (1).

The sharp drop in CL intensity upon the addition of an inhibitor under conditions of continuous feed of O_2 into the solution is due to reaction (4); i.e., when the two stages of DO oxidation proceed simultaneously, the CL is excited in reactions with the participation of oxygen-containing radicals RO_2 or $>AlO_2$.

The residual luminescence that is observed after the decay of CL as a result of adding the inhibitor to the solution is due to reactions of molecular products, one of which is the OAP (thus far, we have not identified any other products).

The authors wish to express their appreciation to R. F. Vasil'ev and V. A. Belyakov for discussions of the results obtained in this work.

CONCLUSIONS

1. The formation of a peroxide in the oxidation of ethylaluminum diethoxide (EtO)₂AlEt in toluene by oxygen proceeds through a free radical mechanism.

2. The chemiluminescence accompanying the process of (EtO)₂AlEt oxidation by oxygen is excited in reactions of two types: free radical and molecular.

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