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Supplementary Material Available: Tables of crystal data, data collection and refinement details, final positional and anisotropic thermal parameters for nonhydrogen atoms, final positional and isotropic thermal parameters for hydrogen atoms, interatomic distances and angles, least-squares planes, and structure factors (12 pages). Ordering information is given on any current masthead page.

Photolysis of Bis(triphenylphosphine)dioxygenplatinum. Generation of Singlet Oxygen

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The majority of thermal reactions of coordination compounds proceeds adiabatically.[1] Only a few nonadiabatic reactions, which may be accompanied by chemiluminescence,[3] have been investigated. On the contrary, all photochemical reactions of transition-metal complexes which are known so far are nonadiabatic since the products seem to be formed in electronic ground states.[4] We report here our observation that the photolysis of $[P(C_6H_5)_3]_2PtO_2$, leading to the release of electronically excited singlet oxygen, is an adiabatic reaction.

While certain organic peroxides are well-known to release singlet oxygen photochemically,[2b,7] the photolyses of some peroxo or dioxygen complexes of transition metals such as $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{4+}$[8] and $[Ir(diphos)_2O_2]^+$[9] also lead to the formation of O_2 but apparently in its triplet ground state.

$[P(C_6H_5)_3]PtO_2$[10] dissolved in organic solvents such as $CHCl_3$ starts to absorb at about 450 nm. The extinction increases toward shorter wavelengths (at 300 nm, ϵ 530). A maximum does not appear until a wavelength of 280 nm where the solvent starts to absorb. When these solutions ($\sim 10^{-3}$ M) saturated with O_2 were irradiated ($\lambda_{irr} > 300$ nm), the complex seemed to be almost stable. When the solutions were deaerated with N_2, light absorption caused a slow decomposition, indicated by a small increase of the optical density between 450 and 300 nm. It was assumed that $[P(C_6H_5)_3]_2PtO_2$ photolyzed to $Pt[P(C_6H_5)_3]_2$ and O_2 in the primary photochemical step. In the presence of excess O_2 the starting complex will be regenerated. In the absence of additional O_2 this recombination seems to be accompanied by an unidentified side reaction, possibly an oxidative addition of the solvent.[11] The formation of $Pt[P(C_6H_5)_3]_2$ as the primary photoproduct was confirmed by low-temperature photolysis. At 77 K the photolysis led to the appearance of a blue emission (λ_{max} = 445 nm) which clearly indicated the generation of $Pt[P(C_6H_5)_3]_2$.[12] The emission intensity increased with irradiation time.

Finally, it was of significance to see whether the photoreleased O_2 was formed in its triplet ground state or an excited singlet state. For the detection of $^1O_2$ we selected 2,2,6,6-tetramethylpiperidine (TMP). It scavenges $^1O_2$ with the formation of a stable nitroxide radical which is easily detectable by ESR spectroscopy at room temperature.[13] The particular advantage of TMP which can be utilized for application in photoreactions is that it does not absorb light at wavelengths longer than 280 nm. In addition, it was shown that the efficiency of $^1O_2$ quenching by TMP derivatives is not very high ($k_q \sim 10^5$ M^{-1} s^{-1}).[13e,14,15] Consequently, the addition of a nonreactive quencher for $^1O_2$ such as the widely used Dabco[14] (1,4-diazabicyclo[2.2.2]octane) with $k_q \sim 2.4 \times 10^7$ M^{-1} s^{-1} should effectively suppress the formation of the nitroxide radical. Such a competition experiment should serve as a further proof for the formation of $^1O_2$.

Upon addition of TMP (2×10^{-3} M) to a solution of $[P(C_6H_5)_3]_2PtO_2$ (2×10^{-3} M) in $CHCl_3$ saturated with N_2, the absorption spectrum of the complex did not change, indicating the absence of a thermal reaction. Upon irradiation (light source: Osram 100 W/2 high-pressure mercury arc; cut-off filter: 310 nm) the extinction of the solution increased between 500 and 300 nm. Simultaneously a strong ESR signal (g = 2.0059, hyperfine coupling 16.15 G) developed which is characteristic for the nitroxide radical of TMP formed by the reaction of TMP with $^1O_2$.[13] This experiment was repeated with Dabco (3×10^{-3}M) added to the solution.[16] The ESR signal now was very weak since Dabco apparently intercepted $^1O_2$.

The formation of $^1O_2$ was confirmed by an additional independent test with 1.3-diphenylisobenzofurane (DIF) as a trap for $^1O_2$[17] DIF scavenges $^1O_2$ with high efficiency ($k_1 = 8 \times 10^8$ M^{-1} s^{-1}). Since DIF is somewhat light sensitive,[7,17] careful control experiments had to be carried out. $[P(C_6H_5)_3]_2PtO_2$ ($\sim 10^{-3}$ M) was irradiated (λ_{irr} = 313 nm) in the presence of DIF ($\sim 4.5 \times 10^{-5}$ M) in a deaerated solution of $CHCl_3$. More than 70% of the incident light was absorbed by the platinum complex. The photolysis was accompanied by a rapid decrease of the absorption maximum at 420 nm, indicating the disappearance of DIF. When DIF was irradiated under identical conditions in aerated or deaerated solutions of $CHCl_3$ in the absence of the complex, only a very slow decrease of the absorption maximum at 420 nm was observed.

In dioxygen complexes of transitions metals electron density is generally shifted from the metal to the dioxygen ligand.[19] This was confirmed by calculations for $(PH_3)_2PtO_2$ which was used as a model for $[P(C_6H_5)_3]_2$ PtO_2.[20] Since the photolysis was accomplished by light absorption into the long-wavelength ab-

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sorption of this complex the lowest energy excited state may initiate the photodissociation. The calculation shows that the lowest energy transition ($7a_2 \rightarrow 19b_2$) is essentially an intraligand (O_2) transition with a ligand-to-metal ($O_2 \rightarrow Pt$) charge-transfer contribution.[20] Consequently, this transition terminates in an excited state with an electronic structure which may be directly related to observed photorelease of electronically excited O_2. Indeed, the $7a_2 \rightarrow 19b_2$ excitation leaves the O_2 ligand almost as neutral as uncoordinated O_2 itself, and the excitation energy resides to a large extent at the O_2 ligand.

The observation that the irradiation of $[Ir(diphos)_2O_2]^+$ leads also to the release of O_2 but in its triplet ground state may be related to the different nature of the reactive excited state. It was suggested that a metal-to-ligand (Ir → diphos) charge-transfer state initiates the photodissociation of the iridium complex.[9] In the case of the cobalt complex mentioned above, the photoactive absorption band[8] was assigned to a ligand-to-metal ($O_2 \rightarrow Co$) charge-transfer transition.[8,21] Also this excitation type is different from that of $[P(C_6H_5)_3]_2PtO_2$. In addition, a comparison between the cobalt and platinum complex seems to be less appropriate due to the different structural features and the bonding modes of O_2 in both complexes.

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Structures of the $C_2H_4O^{+\cdot}$ Gas-Phase Isomers. Evidence for the Formation of the $CH_2OCH_2^{+\cdot}$ Ion from Ethylene Carbonate

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A recent ab initio theoretical study[1] of the structures and stabilities of 11 $C_2H_4O^{+\cdot}$ isomers has shown that the ethylene oxide ion **1** is less stable than its C···C ring-opened isomer **2**, in agreement with measured ΔH_f values,[2] but more stable than the isomer **3** resulting from C···O bond cleavage (Figure 1). In accord with these results we have found[3] that ionized ethylene oxide (**1**) ring-opens to **2** rather than **3**. Kumakura,[4] however, has proposed **3** to be the reactive species in ion/molecule reactions of the ethylene oxide ion. We now report experimental evidence which confirms that, as suggested by theory, the C···O ring-opened isomer **3**, if formed, is not stable but rapidly isomerizes to **2**.

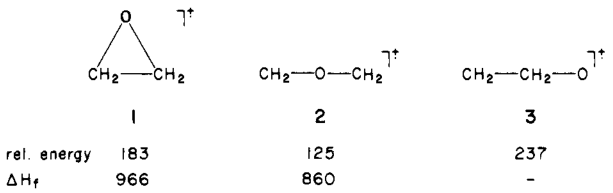
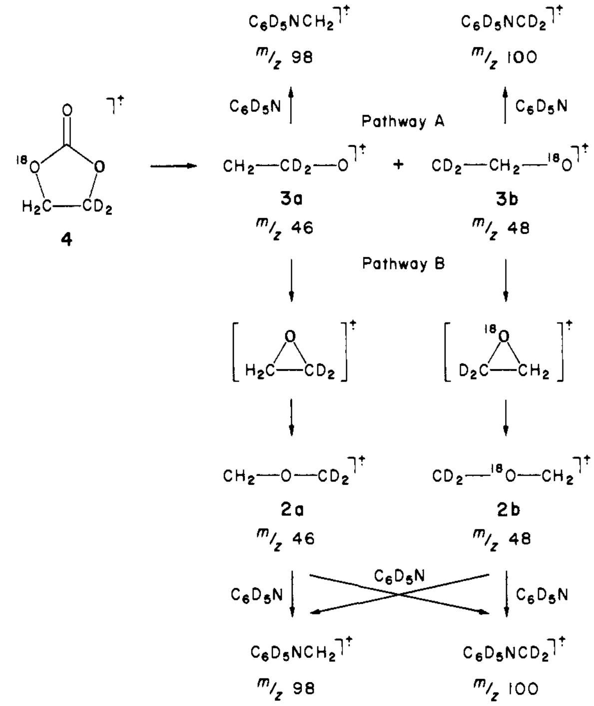
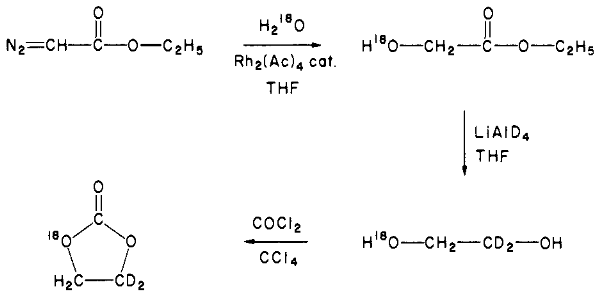


Figure 1. Calculated energies[1] (relative to the most stable isomer $CH_2{=}CH{-}OH^{+\cdot}$) and heats of formation[2] (where measured) in kJ mol^{-1} of three $C_2H_4O^{+\cdot}$ isomers.

Scheme I



Scheme II



As a suitable precursor for isomer **3** we chose 1,3-dioxolan-2-one (ethylene carbonate) which after ionization (**4** unlabeled in Scheme I) readily loses carbon dioxide to give an *m/z* 44 ion ($C_2H_4O^{+\cdot}$).[5] In the ICR spectrometer[6] this fragment ion showed the $CH_2^{+\cdot}$ transfer to neutral pyridine and nitriles typical of isomer **2**.[3] This observation, however, did not in itself prove that isomer **3**, if formed initially, had rearranged to **2** before reacting with a neutral substrate since **3** could equally well be expected to transfer $CH_2^{+\cdot}$ with concomitant formation of neutral formaldehyde.

In order to determine whether the *m/z* 44 ion which was responsible for $CH_2^{+\cdot}$ transfer had the structure **2** or **3**, we prepared (see below) 1,3-[1-^{18}O,4,4-$^2H_2$]dioxolan-2-one as a precursor. Its molecular ion **4** (Scheme I) can lose either $CO^{18}O$ or CO_2 to give two primary fragment ions **3a** (*m/z* 46) and **3b** (*m/z* 48), respectively. On transfer of a methylene radical cation[7] to pyridine-d_5,[8] **3a** would give rise to the product ion *m/z* 98 exclusively, while **3b** would be the only precursor for *m/z* 100 (pathway A). Alternatively, isomerization of **3a** and **3b** to **2a** and **2b**, respectively (pathway B),[9] and subsequent methylene transfer to pyridine-d_5,

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[7] The ICR experiments have shown that no H/D scrambling occurs.

[8] In the experiments with the labeled ethylene carbonate, pyridine-d_5 was used as a neutral substrate in order to avoid overlapping of the product ion peaks with other more intense peaks in the ICR spectrum.