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.

Acknowledgment. Financial support for this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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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

Bruno C. Baumann and John K. MacLeod*

Research School of Chemistry
Australian National University
Canberra, A.C.T. 2600, Australia

Received April 29, 1981

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**.

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

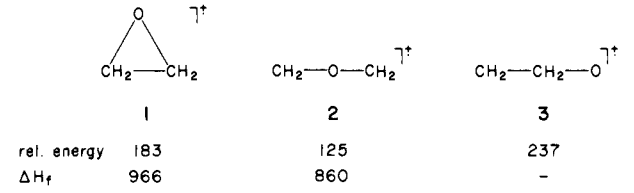
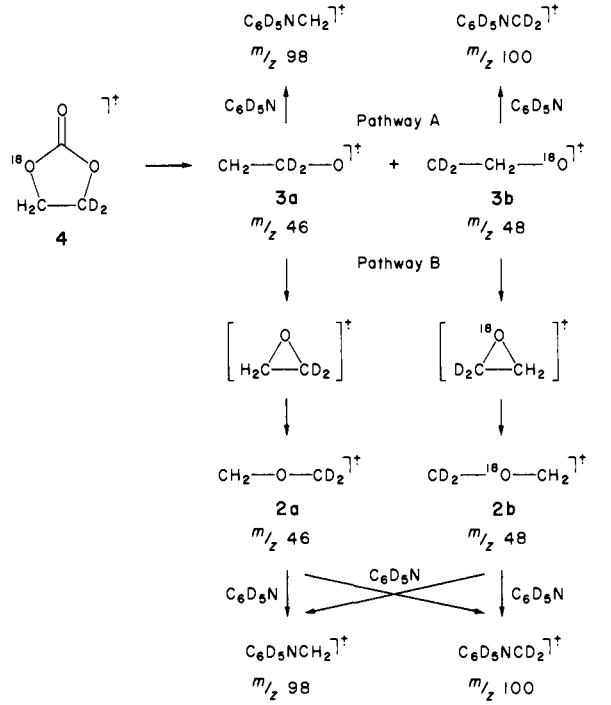
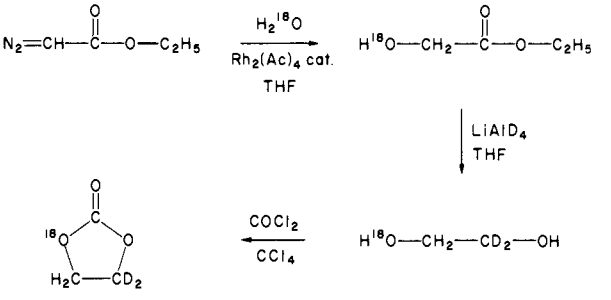


Figure 1. Calculated energies[1] (relative to the most stable isomer $CH_2{=}CH{-}OH^{+\cdot}$) and heats of formation[2] (where measured) in kJ mol^{-1} of three $C_2H_4O^{+\cdot}$ isomers.

Scheme I



Scheme II



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,

(1) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1979**, *101*, 5540–5545.
(2) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860–2862.
(3) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, *724*–725.
(4) Kumakura, M.; Arakawa, K.; Sugiura, T. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 303–320. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 54–57.
(5) Brown, P.; Djerassi, C. *Tetrahedron* **1968**, *24*, 2949–2967.
(6) For general conditions of ICR experiments, see: Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246–2252.
(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.

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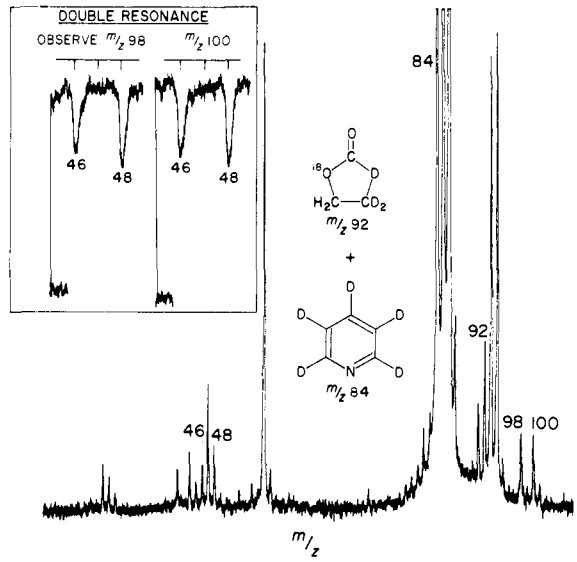


Figure 2. ICR spectrum of a mixture of 1,3-[1-^{18}O,4,4-$^{2}H_2$]dioxolan-2-one and pyridine-d_5.

would lead to the same product ions m/z 98 and 100, each of which would now have both ions, m/z 46 (**2a**) and m/z 48 (**2b**), as precursors.[10]

1,3-[1-^{18}O,4,4-$^{2}H_2$]Dioxolan-2-one was synthesized starting from ethyl diazoacetate as outlined in Scheme II, adapting a published procedure[11] to produce maximum incorporation of the ^{18}O label. The mass spectra of the doubly labeled ethylene glycol and the carbonate confirmed the incorporation (86%, ^{18}O >95% ^{2}H) and location of the labels.

The ICR spectrum[6] of a mixture of 1,3-[1-^{18}O,4,4-$^{2}H_2$]dioxolan-2-one (1.2×10^{-5} torr) and pyridine-d_5[8] (0.3×10^{-5} torr) is shown in Figure 2. Two product ions are observed at m/z 98 and 100 as a result of the transfer of $CH_2^{+\cdot}$ and $CD_2^{+\cdot}$[7] to neutral pyridine-d_5. Double resonance reveals that *each of the two product ions is formed from both precursor ions*, namely, m/z 46 and 48. This result can be explained only by assuming that the primary fragment ions have undergone a rearrangement which, at one stage, has rendered the two methylene groups equivalent. Isomers **1** and **2** are the only $C_2H_4O^{+\cdot}$ ions with equivalent methylene groups. Since **1** has been shown[3] to ring open to **2** prior to the $CH_2^{+\cdot}$ transfer reaction we can conclude that if the $C_2H_4O^{+\cdot}$ isomer **3** is generated from ethylene carbonate[9] it is not stable but undergoes an isomerization yielding, at least in part,[12] isomer **2** (Scheme I). This result is in agreement with the ab initio predictions[1] of the stabilities of the three $C_2H_4O^{+\cdot}$ isomers involved.

Acknowledgment. We thank Dr Leo Radom for his interest in this work.

(9) A referee has pointed out that the $CH_2CH_2O^{+\cdot}$ ion from ethylene carbonate may not even have a transitory existence, but that the cyclic ion **1** may be formed directly, e.g.,

$$\overbrace{OCOOCH_2CH_2}^{}{}^{+\cdot} \rightarrow \cdot OCOOCH_2CH_2^{+} \xrightarrow{-CO_2} \mathbf{1} \rightarrow \mathbf{2}$$

or

$$\overbrace{COOCH_2CH_2O}^{}{}^{+\cdot} \rightarrow \cdot COOCH_2CH_2O^{+} \xrightarrow{-CO_2} \mathbf{1} \rightarrow \mathbf{2}$$

On the available evidence, we cannot rule out this possibility.

(10) A similar approach has been used (Gross, M. L. *J. Am. Chem. Soc.* **1972**, *94*, 3744-3748) to establish that all three methylene groups in the $C_3H_6^{+\cdot}$ ion from tetrahydrofuran, which transfers $CH_2^{+\cdot}$ to NH_3, are identical.

(11) Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssie, Ph. *Tetrahedron Lett.* **1973**, 2233-2236.

(12) Our results do not exclude the possibility that **3** may in part also isomerize to other more stable $C_2H_4O^{+\cdot}$ isomers, e.g., ionized acetaldehyde.[5] Using selective ion/molecule reactions[13] we have, however, not been able to detect any evidence for the isomerization of **3** to $CH_2{=}CH{-}OH^{+\cdot}$ ions.

(13) Bouma, W. J.; MacLeod, J. K.; Radom, L. *Adv. Mass Spectrom.* **1980**, *8*, 178-185.

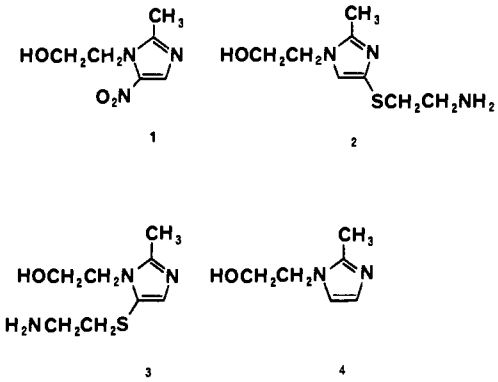
Reactions of Nitroimidazoles. Nucleophilic Substitution of the Nitro Group

P. Goldman* and James D. Wuest*,†

Department of Pharmacology, Harvard Medical School Boston, Massachusetts 02215

Received February 25, 1981

Many heteroaromatic compounds containing a nitro group have antimicrobial properties.[1] One representative of this important class of drugs is 2-methyl-5-nitroimidazole-1-ethanol (metronidazole, **1**), which is clinically effective against trichomoniasis, various forms of amoebiasis, and infections with anaerobic bacteria.[2] Despite the pharmacological importance of the nitroimidazoles, the mechanism of their metabolism and the reason for their selective toxicity toward anaerobic microorganisms have not been determined. Even the chemical behavior of this class of compounds has not been investigated thoroughly. One widely cited mechanism of biological action involves their reduction to radical anions, nitrosoimidazoles or hydroxylaminoimidazoles, followed by interaction of these hypothetical reactive metabolites with cellular macromolecules such as DNA.[3] We report here a series of reactions which emphasize for the first time the susceptibility of these simple nitro heteroaromatic compounds to nucleophilic substitution of the nitro group[4,5] and suggest that this reaction may be the basis for their biological action.



Nitroimidazole **1** reacted readily with 2-aminoethanethiol, which may be considered analogous to the biologically important nucleophile glutathione since both contain a primary sulfhydryl group.[6] At an initial pH of 5.0, the reaction of compound **1** with excess thiol under N_2 (H_2O, 37 °C, 120 h or 100 °C, 1.5 h) produced 4-[(2-aminoethyl)thio]-2-methylimidazole-1-ethanol (**2**, 98%).[7] At pH 9.5 (37 °C, 24 h) the reaction with excess thiol was significantly faster and slightly more complex, leading to compound **2** (45%) as well as to an isomeric thioimidazole, 5-[(2-aminoethyl)thio]-2-methylimidazole-1-ethanol (**3**, 22%).[7] At

† Dépertement de chimie, Université de Montréal, Montréal, Québec, Canada H3C 3V1.

(1) Grunberg, E.; Titsworth, E. *Annu. Rev. Microbiol.* **1973**, *27*, 317.

(2) Goldman, P. *N. Engl. J. Med.* **1980**, *303*, 1212.

(3) Ings, R. M. J.; McFadzean, J. A.; Ormerod, W. E. *Biochem. Pharmacol.* **1974**, *23*, 1421. Mason, R. P.; Holtzman, J. L. *Biochemistry* **1975**, *14*, 1626. Lindmark, D. G.; Müller, M. *Antimicrob. Agents Chemother.* **1976**, *10*, 476. LaRusso, N. F.: Tomasz, M.; Müller, M.; Lipman, R. *Mol. Pharmacol.* **1977**, *13*, 872. Knight, R. C.; Skolimowski, I. M.; Edwards, D. I. *Biochem. Pharmacol.* **1978**, *27*, 2089. Koch, R. L.; Chrystal, E. J. T.; Beaulieu, B. B., Jr.; Goldman, P. *Ibid.* **1979**, *28*, 3611.

(4) For a review of related reactions, see: Beck, J. R. *Tetrahedron* **1978**, *34*, 2057.

(5) For three reports of nitrite displacement from activated derivatives of furan and thiophene, see: Lieb, F.; Eiter, K. *Liebigs Ann. Chem.* **1972**, 761, 130. Dell'Erba, C.; Spinelli, D.; Leandri, G. *Gazz. Chim. Ital.* **1969**, *99*, 535. Dell'Erba, C.; Guanti, G. *Ibid.* **1970**, *100*, 223.

(6) (a) Willson and Searle observed that cysteine and nitroimidazole **1** react under certain conditions, but they did not identify the products of this reaction. See: Willson, R. L.; Searle, A. J. F. *Nature (London)* **1975**, *255*, 498. (b) Under other conditions, however, Boyland and Speyer report that compound **1** does not react with glutathione. See: Boyland, E.; Speyer, B. E. *Biochem. J.* **1970**, *119*, 463. (c) For a review of the chemistry of glutathione, see: Kosower, N. S.; Kosower, E. M. *Int. Rev. Cytol.* **1978**, *54*, 109.

(7) The assigned structure was consistent with the elemental analysis and the IR, NMR, and mass spectra of this new substance.

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