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Mass Spectra and Pyrolyses of Some Vinylene Carbonates

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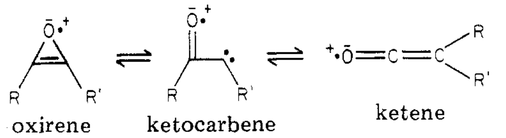
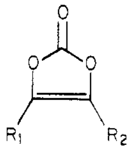
The mass spectra of a series of 1,3-dioxol-2-ones were examined for evidence of oxirenes in the fragmentation process. The $\mathrm{M}^{+\cdot} - \mathrm{CO}_2$ (oxirene or isomers) fragment was observed in six of eight samples. Four major pathways explain the mass spectra: $\mathrm{M}^{+\cdot} - \mathrm{CO}_2 - \mathrm{CO}$, $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_3$, $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_2\mathrm{R}$ and $\mathrm{M}^{+\cdot} - \mathrm{CO} - \mathrm{CO}_2$. Metastable peaks support this. Similar pathways on pyrolysis were sought and observed. At 800 °C and pressure of 1.5–4 mm, 1,3-dioxol-2-ones **1–3** and **5–7** were pyrolyzed in a stream of helium. The major products were, respectively, ketene ($R_1 = R_2 = H$), propene ($R^1 = R^2 = CH_3$), fluorene ($R_1 = R_2 = C_6H_5$), ethene ($R_1 = H$, $R_2 = CH_3$), stilbene ($R_1 = H$, $R_2 = C_6H_5$), and styrene ($R_1 = CH_3$, $R_2 = C_6H_5$). Apparently the 1,3-dioxol-2-ones lose CO_2 and CO successively to produce a carbene which either rearranges or dimerizes.

The mass spectra of a series of 1,3-dioxol-2-ones (vinylene carbonates) were examined for evidence of oxirene in the fragmentation process. Oxirenes have been proposed as intermediates in the peroxidation of acetylenes,[1] in the photolysis of an epoxide[2] ketene,[3] and in the reaction of singlet methylene with carbon monoxide.[4] The most convincing evidence is found in the reports of Strausz and co-workers,[5] who have shown that oxirenes are intermediates in the photolyses of carbon-13 labeled α-diazo ketones. Since the mass spectral data of the 1,3-dioxol-2-ones included fragment ions with the correct m/z values for oxirenes or their isomeric counterparts (eq 1), we decided to investigate the potential of these compounds as precursors or oxirenes by pyrolytic generation. The results of our investigation follow.



(1)

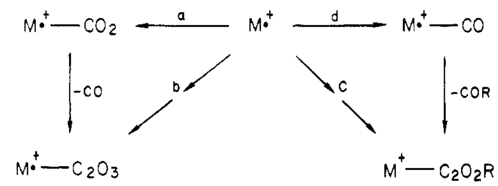
Results and Discussion



1, $R_1 = R_2 = H$
2, $R_1 = R_2 = CH_3$
3, $R_1 = R_2 = C_6H_5$
4, $R_1 = R_2 = Cl$
5, $R_1 = H$; $R_2 = CH_3$
6, $R_1 = H$; $R_2 = C_6H_5$
7, $R_1 = CH_3$; $R_2 = C_6H_5$
8, $R_1 = CH_3$; $R_2 = 3\text{-}CF_3C_6H_4$

Electron-impact fragmentation patterns were obtained on a series of 1,3-dioxol-2-ones (**1–8**) at voltages ranging from 10 to 70 eV. The 70-eV mass spectra are shown in Figures 1–8 (supplementary meterial). Table I summarizes the relative abundances of selected fragments along with observed metastable peaks.

Scheme I



The 1,3-dioxol-2-one molecular ions fragment along four major pathways which are initiated by losses of CO_2, C_2O_3, C_2O_2R, and CO (Scheme I). Pathway a, the loss of CO_2 from parent ions, gives a fragment, which can be represented by the oxirene cation radical and/or its equilibrium isomers (eq 1). Further loss of CO gives the ion $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_3$, which is abundant in the mass spectra of all eight 1,3-dioxol-2-ones. Pathway a is supported by appropriate metastable peaks for compounds **3**, **6**, and **7**. Metastable peaks for compounds **3** and **8** support pathway b; metastable peaks for compound **8** support pathway c. Pathways b and c are almost certainly two-step processes.[6] Although not supported by appropriate metastable peaks, pathway d is probably followed by compounds **1**, **2**, and **5**, each of which shows a $\mathrm{M}^{+\cdot} - \mathrm{CO}$ fragment followed by loss of COR to give $\mathrm{M}^{+} - \mathrm{C}_2\mathrm{O}_2\mathrm{R}$, an abundant ion in all spectra. This fragment can be formed from the parent as well (pathway c). Similarly, DeJongh and Brent[7] reported that *o*-phenylene carbonate and several derivatives fragment along pathways a and d on electron impact and that the $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_3$ ion is the most abundant peak in the mass spectra of three out of four carbonates. We found in our study that the $\mathrm{M}^{+\cdot} - \mathrm{CO}_2/\mathrm{M}^{+\cdot} - \mathrm{CO}$ ratio is rather constant over a 10–70-eV ionizing voltage range, while the $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_3$ and $\mathrm{M}^{+\cdot} - \mathrm{C}_2\mathrm{O}_2\mathrm{R}$ ions increase in relative abundance with increasing ionizing voltage.

The report of Brown and Djerassi[8] describing the electron-impact-induced fragmentations of some cyclic ethylene sulfites and carbonates is particularly germane. They showed that the $\mathrm{M}^{+\cdot} - \mathrm{CO}_2$ ions for cyclic carbonates are most simply represented as ionized aldehydes and ketones that result from pinacol-type rearrangements or as ionized epoxides when phenyl substituents are present.

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(1) (a) Schuback, H.; Franzen, V. *Justig Liebigs Ann. Chem.* **1952**, *60*, 577. (b) franzen, V. *Chem. Ber.* **1954**, *87*, 1478. (c) McDonald, R. N.; Schwab, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 4866. (b) Stille, J. K.; Whitehurst, D. D. *Ibid* **1964**, *86*, 4871. (e) Ciabattoni, J.; Campbell, R. A.; Renner, C. A.; Concannon, P. W. *Ibid.* **1970**, *92*, 3826.

(2) Padwa, A.; Crumrine, S.; Hartman, R.; Layton, R. *J. Am. Chem. Soc.* **1967**, *89*, 4435.

(3) Russel, R.; Rowland, F. S. *J. Am. Chem. Soc.* **1970**, *92*, 7508.

(4) Montague, D.; Rowland, F. S. *J. Am. Chem. Soc.* **1971**, *93*, 5581.

(5) Fenwick, J.; Frater, G.; Ogi, K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 124 and references therein.

(6) Meyerson, Vander Haar, and Fields (Meyerson, S.; Vander Haar, R. W.; Fields, E. K. *J. Org. Chem.* **1972**, *37*, 4114) argue that the often used assumption that metastable peaks denote a single reaction step is not justified by fact or theory.

(7) DeJongh, D. C.; Brent, D. A. *J. Org. Chem.* **1970**, *35*, 4204.

(8) Brown, P.; Djerassi, C. *Tetrahedron* **1968**, *24*, 2949.

0022-3263/82/1947-0702$01.25/0

Table I. Percent Relative Abundances of Selected Fragment Ions and m/z Values for Metastable Ions from 1,3-Dioxol-2-ones at 70 eV

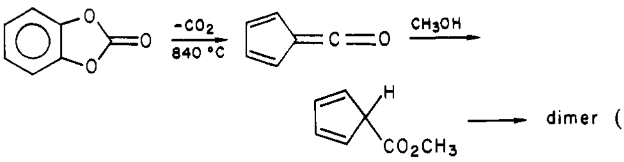
		rel abundance, %				
compd	m/z for m*	$M^{+\cdot}$	$M^{+\cdot} - CO$	$M^{+\cdot} - CO_2$	$M^{+\cdot} - C_2O_3$	$M^+ - C_2O_2R$
1		91	33	58	67	100
2		31	4	6	29	100
3[a]	74, 116, 142, 158	39			47	20
4[b]		61			100	61
5		70	4	10	100	83, 45 ($R = H, CH_3$)
6	69, 86	59		7	100	9, 5 ($R = H, C_6H_5$)
7	82, 99	100		4	67	20, 24 ($R = CH_3, C_6H_5$)
8	62, 122, 145, 164	56		7	100	34, 48 ($R = CH_3$, m-$C_6H_4CF_3$)

[a] m* was obtained at 15 eV; m* was not observed at 70 eV; $M^{+\cdot} - CO_2$ was observed at 15 eV. [b] ^{35}Cl isomers.

We envisage the 1,3-dioxol-2-ones (cyclic vinylene carbonates) of this study as undergoing loss of CO_2 to form a ketocarbene radical cation ($RCOCR'^{+\cdot}$) analogous to the ionized ketones and aldehydes cited by Brown and Djerassi.[8] The ketocarbene radical cation can rearrange to a ketene or to an oxirene (eq 1) which is analogous to the "epoxide-like" ($M^{+\cdot} - CO_2$) ions described by Brown and Djerassi.[8]

The electron-impact data ($M^{+\cdot} - CO_2$) indicates the possibility of generating oxirenes from 1,3-dioxol-2-ones by the other kinds of high-energy interactions, namely, pyrolysis and photolysis. Dougherty[9] extended Dewar's perturbation method[10] to radical cations and examined the relationship between mass spectrometric, thermal, and photolytic fragmentation reactions on this basis. Prominent among many research groups which have studied the empirical relationships between mass spectrometric and thermolytic reactions are those of DeJongh and co-workers and Fields and Meyerson.[11]

On electron impact, alkyl phenyl and aryl phenyl carbonates suffer direct loss of CO_2 from the molecular ion, while dialkyl carbonates undergo a rearrangement prior to loss of CO_2.[12] Pyrolysis of ethyl aryl carbonates yields CO_2, C_2H_4, and the corresponding phenol.[13] Having noted the similarities in the above processes, DeJongh and Brent[7] examined the pyrolytic and electron-impact reactions of o-phenylene carbonate. They found similarities. A $C_6H_4O^{+\cdot}$ fragment($M^{+\cdot} - CO_2$) is prominent in the mass spectrum. Pyrolysis at 840 °C, under trapping conditions with methanol, produced a 34% yield of methyl cyclopentadiene-1-carboxylate, indicating the presence of a ketene (C_6H_4O) in the pyrolysate (eq 2).



(2)

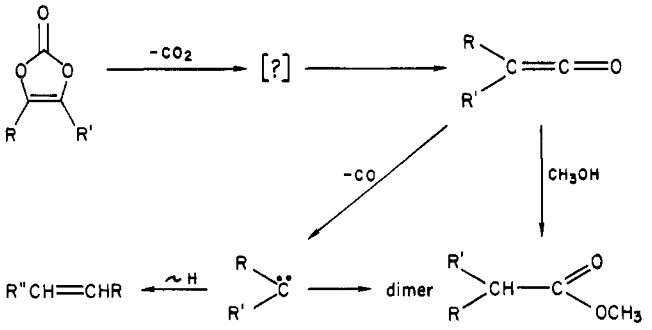
Having established that 1,3-dioxol-2-ones follow pathway a on electron impact (though not exclusively), we hoped to find a similar pathway on pyrolysis. 1,3-Dioxol-2-ones 1–3 and 5–7 were pyrolyzed at 800 °C in a stream of helium in a quartz tube at pressures up to 2.5 mm. the products were trapped and analyzed by GC/MS or other spectroscopic methods. In each pyrolysis, methanol was added to a trap in an effort to capture ketene products as methyl esters. A summary of results is detailed in Table II.

Table II. Pyrolysis Results[a]

		products[b]	
reactant[e]	ketene adduct[c]	major	minor[d]
1	yes	ketene	
2	no	propene	ethyne
3	no	fluorene	
5	no	ethene	
6	no	stilbene	biphenyl
7	no	styrene	

[a] Quartz tube at 800 °C, pressure 2.5 mm, He flow 0.7–0.9 L/min. [b] Carbon monoxide not retained by liquid N_2 trap. [c] Methanol added to liquid N_2 trap to capture ketenes. [d] Other minor products from pyrolysis of 6 are detailed in the Experimental Section. [e] CO_2 found in all cases.

Scheme II



A summary of the predominant pathway for pyrolysis of 1,3-dioxol-2-ones follows in Scheme II. In only one case were we able to capture a ketene intermediate, 1,3-dioxol-2-one. We presume that at 800 °C all other ketenes decarbonylate to carbenes which rearrange and/or dimerize. Aside from the report of DeJongh and Brent[7] on o-phenylene carbonate (benzo-1,3-dioxol-2-one; see above), no other pyrolysis work on 1,3-dioxol-2-ones has appeared in the literature. Pyrolysis of ketene[14] and methylketene[15] (intermediates in our pyrolysis scheme) have been looked at however.

Our results show that 1,3-dioxol-2-ones undergo thermal and electron-impact decomposition along similar pathways, i.e., successive losses of CO_2 and CO. The ketene precursors could be the elusive oxirenes. At lower pyrolysis

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(9) Dougherty, R. C. *J. Am. Chem. Soc.* **1968**, *90*, 5780.

(10) (a) Dewar, M. J. S. *Tetrahedron Suppl.* **1966**, *8*, 75. (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341, 3345, 3350, 3353, 3355, 3357.

(11) (a) DeJongh, D. C.; VanFossen, R. Y.; Bourgeois, C. F. *Tetrahedron Lett.* **1967**, 271. (b) Brent, D. A.; Hribar, J. D.; DeJongh, D. C. *J. Org. Chem.* **1970**, *35*, 135. (c) Fields, E. K.; Meyerson, S. *J. Am. Chem. Soc.* **1966**, *88*, 2836 and papers cited therein.

(12) (a) Brown, P.; Djerassi, C. *J. Am. Chem. Soc.* **1966**, *88*, 2469. (b) *Ibid.* **1967**, *89*, 2711.

(13) Smith, G. G.; Koesters, B. *Chem. Ber.* **1960**, *93*, 2400.

(14) (a) Tsuda, M.; Kuratami, K. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 53. (b) Muller, J. A.; Peytral, E. *C. R. Hebd. Seances Acad. Sci.* **1933**, *196*, 279. (c) Guenther, W. B.; Walters, W. D. *J. Am. Chem. Soc.* **1959**, *81*, 1310. (d) Young, J. R. *J. Chem. Soc.* **1958**, 2909.

(15) Blake, P. G.; Hole, K. J. *J. Phys. Chem.* **1966**, *70*, 1464.

temperatures it might be possible to capture them. We will be investigating that possibility.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer 337 spectrophotometer. NMR spectra were obtained on a Varian A-60 spectrometer. Samples were neat or dissolved in CCl_4 or $CDCl_3$ with 1% Me_4Si as an internal standard. All GC work was performed on an Aerograph Autoprep Model A-700 with a thermal-conductivity detector or a Hewlett-Packard 5750 with flame-ionization detection. Electron-impact spectra were measured on a 270B Perkin-Elmer mass spectrometer, where gases and liquids were analyzed via a gas chromatograph inlet; the solids were analyzed via the solids probe inlet. Separation of gases and liquids for mass analyses was accomplished by using a 6 ft × $^{1}/_{8}$ in. copper column of Chromosorb 104 (60/80 mesh) and an 8 ft × 0.25 in. column of 1.5% OV-17 on Chromosorb W-AW-DMCS (60/80 mesh) at temperatures ranging from 45 to 220 °C. Experimental mass spectral fragmentation patterns were compared with those available in ref 16. 1,3-Dioxol-2-one was obtained from Aldrich Chemical Co. and was checked for purity by NMR spectrometry before use. 1,3-Dioxol-2-ones **2**–**8** are known carbonates which were synthesized and purified as outlined in ref 17.

Pyrolysis Apparatus. A stream of helium is passed through a liquid N_2 trap, and the flow rate is monitored with a rotometer before passing it over a heated sample in a distilling flask. The helium entrained sample is directed into a 24 × 1 in. (i.d.) hollow quartz tube, which is surrounded by a 12-in. Lindberg electric furnace equipped with a thermocouple touching the center of the quartz tube on the outside. The exit gases are first passed through a stopcock, which isolates the pyrolysis chamber from the vacuum, and then into a liquid N_2 cooled gas trap connected by a three-way valve to a gas bulb and open-end manometer in series and to the rest of the vacuum line. A second liquid N_2 gas trap, a leak valve, a McLeod Gauge, and the vacuum pump are positioned in series from the three-way valve.

Pyrolysis Procedure. The distilling flask and sample are cooled with dry ice–acetone bath while two evacuate–fill cycles are carried out on the entire system with helium. Thereafter, a helium flow rate of 0.7–0.9 L/min at 1.5–4 mm is established while the quartz tube is brought to 800 °C. When the quartz tube reaches operating conditions, the gas sampling bulb and open-end manometer are isolated from the system, liquid N_2 is added to the traps, and the dry ice–acetone bath is removed from the sample to be pyrolyzed. Usually a heated oil bath is needed to vaporize the sample. When pyrolysis is complete, the first liquid N_2 trap (which contains the pyrolysate), the gas bulb, and the manometer are isolated from the system. Removal of the liquid N_2 trap allows liquuified gas samples to expand into the gas samping bulb from which they can be analyzed by GC/MS. Contents of the trap that remain liquid or solid at room temperatures are analyzed appropriately.

Pyrolysis Results. 1,3-Dioxol-2-one. A 5.22-g sample of **1** was pyrolyzed at 800 °C (1.4 mm) to produce CO_2 and ketene, identified by mass spectral fragmentation patterns, retention times, and by H_2O/CH_3OH derivatization in separate pyrolysis experiments. The acetic anhydride and methyl acetate derivatives were identified by IR and NMR spectrometry.

4,5-Dimethyl-1,3-dioxol-2-one. A 1.81-g sample of **2** was pyrolyzed at 800 °C (1.2 mm) to produce CO_2, propene, and acetylene in a ratio of 100:38:2.4 as determined by GC/MS. A dimethylketene-CH_3OH adduct was not observed.

4,5-Diphenyl-1,3-dioxol-2-one. a 2.18-g sample of **3** was pyrolyzed at 800 °C (1.45 mm) to produce CO_2 as the only gaseous product. A solid product, shown to be fluorene by IR, NMR, and mass spectra, melting point, and elemental analysis, was isolated in 31% yield after recyrstallization. A small amount of an orange liquid was unidentified. A diphenylketene–CH_3OH adduct was not observed.

4-Methyl-1,4-dioxol-2-one. A 0.985-g sample of **5** was pyrolyzed at 800 °C (2.5 mm) to produce CO_2 and ethylene in a ratio of 57:43 as determined by GC/MS. Two minor gaseous components were unidentified. A methylketene–CH_3OH adduct was not observed.

4-Phenyl-1,3-dioxol-2-one. a 2.02-g sample of **6** was pyrolyzed at 800 °C (1.5 mm) to produce CO_2 as the only gaseous component and a liquid containing at least nine components.[18] When subjected to GC/MS analysis, the following compounds (in order of elution from Chromosorb 104) were identified (percent composition in parentheses): styrene (1%), benzaldehyde (1%), methylphenylacetylene or indene (3%), naphthalene or azulene (9%), biphenyl (17%), 1-allylnaphthalene or diphenylmethane (13%), stilbene (37%), unknown a (14%), unknown b (5%). A phenylketene–CH_3OH adduct was not observed.

4-Methyl-5-phenyl-1,3-dioxol-2-one. a 0.395-g sample of **7** was pyrolyzed at 805 °C (1.5 mm) to produce CO_2 as the only gaseous component and a liquid identified as styrene as determined by IR, NMR, and GC/MS. A methylphenylketene–CH_3OH adduct was not observed.

Acknowledgment. Early in the investigation the mass spectra were obtained from Dr. Don C. DeJongh and Mr. Laurence R. Dusold at the facilities of Wayne State University. We thank them and Dr. Sara J. Melford of DePaul University for her assistance throughout the investigation. Dr. DeJongh was kind enough to read the manuscript and make comments.

Registry No. 1, 872-36-6; **2**, 37830-90-3; **3**, 21240-34-6; **4**, 17994-23-9; **5**, 4427-89-8; **6**, 16761-08-3; **7**, 40352-53-2; **8**, 53601-86-8.

Supplementary Material Available: Bar graphs representing the mass spectra of compounds **1**–**8** (Figures 1–8) (8 pages). Ordering information is given on any current masthead page.

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(16) Stenhagen, F.; Abrahamson, S.; McLafferty, F. W. "Registry of Mass Spectra Data"; Wiley: Ithaca, NY, 1964; Vol. I.

(17) Breitbeil, F. W.; Wright, L.; Foss, T. H.; LaRose, R. C. *Trans. Ill. State Acad. Sci.* **1974**, *67*, 139.

(18) The mass spectra of several components are almost indistinguishable from at least two reference spectra published in ref 16 so that we cannot make a positive identification; e.g., indene or methylphenylacetylene on p 157.