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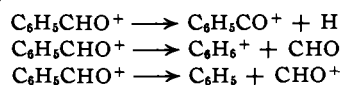
Organic Ions in the Gas Phase. X. Decomposition of Benzaldehyde under Electron Impact

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Label retention in fragments from benzaldehyde- α - d , - o - d and - m - d ionized by electron impact is consistent with loss of the formyl group without prior rearrangement of the molecule-ion. Gross differences between ionic decomposition paths of benzaldehyde and the isomeric tropone show that primary interconversion between these compounds is unimportant. These results contrast sharply with the behavior of toluene and cycloheptatriene, which decompose predominantly *via* common ionic intermediates.

Considerable evidence suggests that benzene derivatives tend to rearrange, upon ionization in the gas phase at low pressures, to structures with a seven-membered ring.¹ On the contrary, major features, at least, of the mass spectrum of benzaldehyde² can apparently be accounted for without postulating ring expansion. Appearance potentials of the $C_7H_5O^+$, $C_6H_5^+$ and CHO^+ ions have been interpreted³ on the assumption that they are formed from the unrearranged parent ion by the reactions



Seeking further evidence on ionic decomposition of benzaldehyde induced by electron impact, we have studied the mass spectra of this compound unlabeled and labeled with deuterium in the *alpha*, *ortho* and *meta* positions, and of tropone, an isomer of benzaldehyde containing a seven-membered ring. Label retentions and metastable peaks, supplemented by correlation of the spectra and structures of the isomeric compounds, were used to help define the reaction paths involved.¹

Experimental

Unlabeled benzaldehyde was kindly furnished by E. L. Eliel of the University of Notre Dame; tropone, by H. J. Dauben, Jr., L. R. Honnen and J. G. Shdo of the University of Washington. Color that had developed in the tropone was removed—as well as a trace of benzene, the only impurity detected in the chromatogram—by gas chromatography. The deuterated benzaldehydes were prepared by reaction of deuterated benzyl chlorides, available from another investigation,⁴ with hexamethylenetetramine, followed by hydrolysis in boiling water⁵; products were separated by gas chromatography.

The usual low-voltage technique for measuring isotopic composition⁶ failed because no value of ionizing voltage could be found great enough to produce a useful intensity of benzaldehyde parent ions, but still low enough to produce no parent-less-H ions.⁷ Isotopic purities of the ring-deuterated benzaldehydes were assumed equal to those of the corresponding chlorides used in the syntheses. That of the α - d species was assumed equal to that of the chloride- α - d_2 plus half the concentration of the d_1 impurity. Isotopic purities thus arrived at are: α - d , 98.1%; o - d , 88.2%; m - d , 80.5%.

Mass spectra of the benzaldehydes were measured with 70-volt electrons on a Consolidated model 21-103c instrument, the sample-introduction system of which was operated at room temperature. Partial spectra are shown in Table I, corrected for unlabeled benzaldehyde in the labeled materials and for naturally occurring heavy isotopes of carbon, hydrogen and oxygen.⁸

(1) H. M. Grubb and S. Meyerson, in "The Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 453.

(2) Manufacturing Chemists Association, "Catalog of Mass Spectral Data," Chemical Thermodynamics Properties Center, Agricultural and Mechanical College of Texas, College Station, Texas, 1959-1962, Ser. No. 83.

(3) R. I. Reed and M. B. Thornley, *Trans. Faraday Soc.*, **54**, 949 (1958).

(4) S. Meyerson, P. N. Rylander, E. L. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(5) K. B. Wiberg, *Org. Syntheses*, **29**, 87 (1949).

(6) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

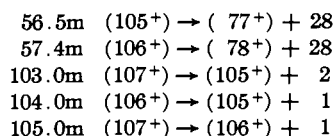
(7) This finding implies that the appearance potentials of $C_7H_5O^+$ and $C_7H_5^+$ are nearly equal and is inconsistent with the large difference between the reported values 9.63 and 11.21 e.v.³

(8) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1960.

TABLE I
PARTIAL SPECTRA OF BENZALDEHYDES^a

<i>m/e</i>	Unlabeled	α - d	o - d	m - d
29	15.3	0.7	15.2	15.5
30	...	17.2
56.5m	0.4	0.4
57.4m	0.5	0.5
77	117.2	100.2	5.8	6.0
78	15.5	7.0	116.7	116.9
79	0.1	18.0	19.9	20.9
103.0m	...	0.7
104	} 1.8	0.1	0.1	0.1
104.0m	
105	106.4	100.2	} 1.8	} 1.4
105.0m		
106	100.0	0.7	107.0	106.4
107	...	100.0	100.0	100.0

Metastable transitions

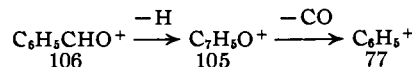


^a Metastable peaks are denoted by m.

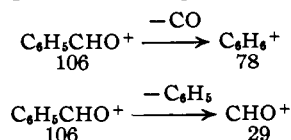
Repeated attempts to admit tropone to the room-temperature instrument failed; essentially no pressure rise was indicated in either the inlet system or the exhaust line, and the mass spectrum showed only water, even when the tropone was first passed through a tube filled with Drierite. Apparently, tropone is polar enough that it was adsorbed quantitatively on the glass and stainless steel walls of the sample-introduction system, displacing adsorbed water in the process.⁹ The material was admitted and the spectrum measured with no difficulty on a "high-mass" spectrometer, a modified¹⁰ Consolidated model 21-103c instrument with the sample-introduction system heated to 250°. Figure 1 shows the spectra of benzaldehyde and tropone, both measured on this instrument with 70-volt electrons. Inspection of the spectrum of tropone suggested that it is related to that of benzene; the latter, measured on the same instrument, is therefore included in Fig. 1. These spectra have not been corrected for heavy-isotopic contributions.

Mass Spectra of Labeled Benzaldehydes

The data in Table I establish the major decomposition path



and strongly suggest two competing primary reactions



Relative intensities at corresponding masses in the four spectra agree reasonably well. The spectrum that deviates most markedly on this score is that of the α - d species. Such deviation, attributed to

(9) Compare S. Meyerson, *Anal. Chem.*, **28**, 317 (1956).

(10) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

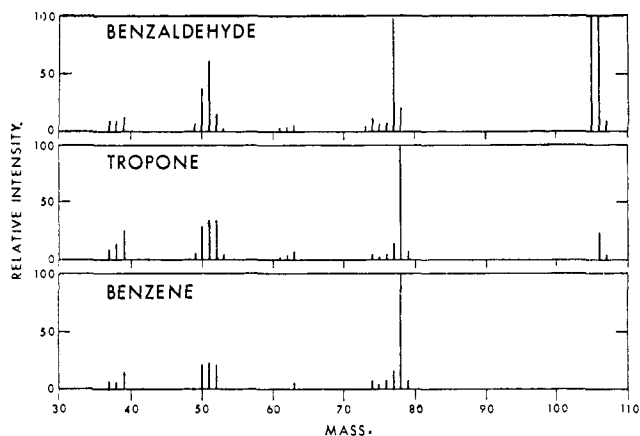
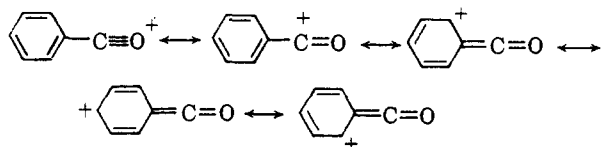


Fig. 1.—Mass spectra.

isotope effects in the underlying reactions, implies clearly that the hydrogen atom on the α -carbon remains chemically distinct in the reacting parent ion from those on ring carbons. Mutual consistency of the spectra of the four isotopic benzaldehydes supports the belief that no serious error was incurred in estimating isotopic purities from those of the precursor benzyl chlorides.

The $C_7H_5O^+$ Ion.—Label retentions in $C_7H_5O^+$ —essentially 0, 100 and 100% in the α -*d*, *o*-*d* and *m*-*d* species, respectively—and the associated metastable peaks establish that the hydrogen atom lost comes solely from the α -position. The isotope effect evidenced by the reduced $C_7H_5O^+ : C_7H_6O^+$ intensity ratio in the spectrum of benzaldehyde- α -*d* parallels that observed in the rate-determining step—rupture of the α -C-H bond—in oxidation of benzaldehyde by neutral permanganate.¹¹

The ion may be represented by the resonance-stabilized benzoylium ion^{12,13}



Such a stable species, which seems to exist also in solution,¹⁴ can account for the high $C_7H_5O^+$ intensity typical of the spectra of compounds containing the benzoyl group.^{13,15,16} Moreover, this structure seems consistent with the subsequent loss of CO evidenced by metastable peaks in the spectra of the isotopic benzaldehydes and of alkyl phenyl ketones.^{15,17} High parent-less-H:parent intensity ratios, approaching that of benzaldehyde, are characteristic of substituted benzaldehydes,^{16,18} as well as of the lower aliphatic aldehydes,¹⁹ but rare in most other classes of compounds. Apparently, primary loss of the α -hydrogen atom in the formyl group persists as a dominant reaction despite the presence of other functional groups in the molecule.

The $C_6H_5^+$ Ion.—The $C_6H_5^+$ ion, corresponding to loss of CO from the parent ion, necessarily contains

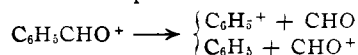
- (11) K. B. Wiberg and R. Steward, *J. Am. Chem. Soc.*, **77**, 1786 (1955).
- (12) E. L. Eliel, J. D. McCollum, S. Meyerson and P. N. Rylander, *ibid.*, **83**, 2481 (1961).
- (13) F. W. McLafferty, in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Vol. 2, Academic Press, Inc., New York, N. Y., 1962, p. 93.
- (14) R. J. Gillespie, *J. Chem. Soc.*, 2997 (1950).
- (15) S. Meyerson and P. N. Rylander, *J. Am. Chem. Soc.*, **79**, 1058 (1957).
- (16) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **34**, 33 (1962).
- (17) S. Meyerson and J. D. McCollum, unpublished spectra.
- (18) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33**, 386 (1961).
- (19) J. A. Gilpin and F. W. McLafferty, *ibid.*, **29**, 990 (1957).

all six original hydrogen atoms. Actually, relative intensities of $C_6H_5D^+$ in the spectra of the three deuterated benzaldehydes are somewhat higher than that of $C_6H_6^+$ in the spectrum of the unlabeled species. The deuterium atom seems to stabilize this ion, reducing the extent of further decomposition. Similarly, the parent ion of benzene is apparently stabilized by deuterium substitution. For example, the intensity of $C_6H_5D^+$ from benzene-*d*₁,²⁰ relative to the summed intensities of all six-carbon ions, is 1.02 times as great, and that of $C_6D_6^+$ from perdeuteriobenzene²¹ is 1.11 times as great, as that of $C_6H_6^+$ from unlabeled benzene.

The CHO^+ Ion.—Label retention in CHO^+ from benzaldehyde- α -*d* is 100%; from ring-deuterated species, it is zero. This ion undoubtedly contains the elements of the original side chain, and is therefore almost certainly formed in a primary decomposition. Such a process has a close parallel in the ionization-dissociation of benzyl alcohol to produce a CH_2O^+ ion containing the elements of the original side-chain.¹² Both contrast sharply with formation from toluene of CH_3^+ containing, on the average, two hydrogen atoms derived from the original side chain and one from the ring.²²

The CHO^+ ion is prominent in the spectra of the lower aliphatic aldehydes¹⁹ and is even more prominent in those of the aldehydes RCHO in which R is perfluoromethyl,²³ -ethyl²⁴ and -propyl.²⁴ The connecting links between the large number of fluorine atoms and the enhanced yield of CHO^+ in the spectra of the fluorinated aldehydes may be lower α -bond strength and increased charge localization in the carbonyl group of the molecule-ion, caused by high electronegativity of the perfluoroalkyl groups. The observed correlation accords with the idea that charge localization is intimately associated with chemical activity and that distribution of the charge within the ionized molecule exerts a critical influence on the mass spectrum.^{1,13,25,26}

The $C_6H_5^+$ Ion.—Metastable peaks shown in Table I establish consecutive loss of H and CO as one path of formation of $C_6H_5^+$. Primary dissociation of the parent ion to $C_6H_5^+$ and CHO, as was assumed³ in interpreting the appearance potential of $C_6H_5^+$, is also a likely contributing path. The latter reaction is complementary to formation of CHO^+ ; distribution of charge between the products of the dissociation



should be a function of the difference between the ionization potentials of C_6H_5 and CHO.²⁷ Literature values place the ionization potentials of formyl²⁸ and phenyl²⁹ radicals close together. If they are in fact nearly equal, then primary cleavage of the phenyl-formyl bond should contribute strongly to the yield of $C_6H_5^+$ as well as to the observed substantial yield of CHO^+ . Both paths would lead to label retentions in $C_6H_5^+$ of zero from benzaldehyde- α -*d* and 100%

(20) American Petroleum Institute Research Project 44, "Catalog of Mass Spectral Data," Chemical Thermodynamics Properties Center, Agricultural and Mechanical College of Texas, College Station, Texas, 1947-1962, Ser. No. 538.

(21) S. Gordon and M. Burton, *Discussions Faraday Soc.*, **12**, 88 (1952).

(22) P. N. Rylander and S. Meyerson, *J. Chem. Phys.*, **27**, 1116 (1957).

(23) R. E. Dodd and J. W. Smith, *J. Chem. Soc.*, 1465 (1957).

(24) G. H. Miller and G. O. Pritchard, *Chem. Ind. (London)*, 1314 (1961).

(25) J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(26) F. W. McLafferty, in "Advances in Mass Spectrometry," J. D. Waldron, Ed., Pergamon Press, New York, N. Y., 1959, p. 355.

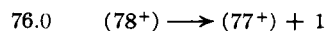
(27) S. Meyerson and J. D. McCollum, *Advan. Anal. Chem. Instrumentation*, in press.

(28) R. I. Reed, *Trans. Faraday Soc.*, **52**, 1195 (1956), R. I. Reed and J. C. D. Brand, *ibid.*, **54**, 478 (1958).

(29) R. J. Kandel, *J. Chem. Phys.*, **22**, 1496 (1954).

from ring-labeled species. Observed retentions of 6.5% from the α -isomer and about 100% from the *ortho* and *meta* are consistent with either or both of the above paths as the source of most of the $C_6H_5^+$ yield.

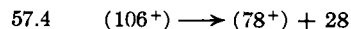
That the label is retained in even a small part of the $C_6H_5^+$ yield from benzaldehyde- α -*d* implies the existence of yet another contributing path. A metastable peak



in the spectrum of unlabeled benzaldehyde, not detected in the spectrum shown in Table I but clearly visible in the one measured on the high-mass instrument, identifies $C_6H_5^+$ as another $C_6H_5^+$ precursor. If the six hydrogen atoms in $C_6H_5D^+$ lose positional identity, 83%—neglecting possible isotope effects—of the $C_6H_5^+$ ions arising from this precursor should retain the label.

Comparison with Tropone

Comparison of the spectra of benzaldehyde and tropone supports the view that most fragment ions from the former arise by paths not involving ring expansion. The spectra differ markedly—a rather different state of affairs from that found with toluene, cycloheptatriene and the four other C_7H_8 isomers, the mass spectra of which have been reported.¹ Loss of a hydrogen atom to form $C_7H_7O^+$ contributes but little to the spectrum of tropone. The most abundant ion is $C_6H_6^+$, shown by the metastable peak



to arise by loss of CO from the parent ion. The many similarities in the spectra of tropone and benzene—especially the profiles at *m/e* 50 to 52 and 73 to 78—suggest that most of the smaller fragment ions formed from tropone stem from a $C_6H_6^+$ intermediate and, indeed, that common states of $C_6H_6^+$ are involved in decomposition of tropone and benzene.

The reaction apparently occurring in tropone—two C—CO bonds rupturing and a new bond forming across the gap from which CO is lost—seems to occur also in benzotropone and in many quinones and aromatic ketones in which the carbonyl group is incorporated in a ring,^{26,30,31} but little or no loss of CO occurs from the parent ions of aliphatic aldehydes.¹⁹ Loss of CO from benzaldehyde may arise from a ring-expanded, tropone-like intermediate. The driving force for other decomposition paths in benzaldehyde is evidently centered in the carbonyl group; ring expansion in $C_6H_6^+$ formation would parallel the behavior of other benzene derivatives and thus reflect the influence of the benzene ring.

(30) J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **14**, 156 (1960).

(31) In cycloalkanones, in contrast, loss of CO is slight. High-resolution measurements show that the ions of parent mass less 28 units in the spectra of these compounds arise chiefly by loss of C_2H_4 [J. H. Beynon, R. A. Saunders and A. E. Williams, *Appl. Spectry.*, **14**, 95 (1960)], paralleling the loss of C_2H_4 from cycloalkanes [S. Meyerson, T. D. Nevitt and P. N. Rylander, in "Advances in Mass Spectrometry," Vol. 2, R. M. Elliott, Ed. Pergamon Press, New York, N. Y., 1963, p. 313].

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Kinetics and Mechanisms of the Hydrolysis of Some Chloroamminerhodium(III) Complexes^{1,2}

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The rates of hydrolysis of certain chloroamminerhodium(III) complexes were investigated as a function of steric effects, the extent of chelation and other variables. It was observed that various nucleophiles have no effect on the rate of chloride ion release from these systems. These results are similar to the behavior of analogous cobalt(III) systems. Striking differences were also found: (1) the rate of reaction of a rhodium(III) complex is insensitive to the charge on the complex, (2) alkali has little or no effect on the rate of hydrolysis and (3) reactions of rhodium(III) complexes occur with almost complete retention of configuration. These results are discussed in terms of probable mechanisms for reactions of rhodium(III) complexes.

Introduction

The literature contains numerous descriptions of the reactions of the ammine complexes of cobalt(III). The diacidotetraammines, $[CoA_4X_2]^+$, and the acidopentaammines, $[CoA_5X]^2+$, have been of particular interest.⁴ Extensive studies of the rates of hydrolysis of the complexes $[CoA_4X_2]^+$ and $[CoA_5X]^2+$ have been made as a function of a large number of variables.⁵

It is, therefore, somewhat surprising that so little information has appeared on the analogous complexes of the second and third row transition element members of the cobalt triad, rhodium and iridium. It would certainly be of interest to ascertain the effect of increasing size and effective nuclear charge of the central metal atom upon the reactions of the various complex

ions. The only quantitative kinetic studies of the reactions of acidoamminerhodium(III) and -iridium(III) complexes are those reported by Lamb⁶ for $[Rh(NH_3)_5Cl]^{2+}$ and $[Rh(NH_3)_5Br]^{2+}$ and by Lamb and Fairhall⁷ for $[Ir(NH_3)_5X]^{2+}$, X = Cl^- , Br^- , I^- and NO_3^- .

The dearth of information available on the reactions of diacidotetraamminerhodium(III) complexes may be logically ascribed to the fact that until very recently⁸ only a few isolated members of this group had been prepared. Any study of those compounds whose syntheses had been described would have precluded all but the sketchiest of comparisons to the members of the very prolific cobalt(III) family; indeed no examples of either geometric or optical isomerism were known. The successful synthesis of many of the necessary diacidotetraamminerhodium(III) complexes now makes possible quantitative comparisons between these systems and the analogous cobalt(III) compounds. This paper reports kinetic data on reactions of rhodium(III) systems and discusses these data in terms of the previously reported results on cobalt(III).

(1) This research was supported in part by the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)315, and in part by the U. S. Atomic Energy Commission under contract AT(11-1)-1087.

(2) Taken in part from the Ph.D. Thesis of S. A. Johnson, Northwestern University, 1961.

(3) National Institutes of Health Fellow, 1960–1961.

(4) In these general formulas, A_4 and A_5 indicate coordination to cobalt of four and five amine nitrogens, respectively; X represents a mononegative anion such as Cl^- , Br^- , I^- , CNS^- , N_3^- , NO_2^- or OH^- .

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, Chapter 3.

(6) A. B. Lamb, *J. Am. Chem. Soc.*, **61**, 699 (1939).

(7) A. B. Lamb and L. T. Fairhall, *ibid.*, **45**, 378 (1923).

(8) S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).