# 3,5-Dimethylphenol and Other Products from Pyrolysis of Sodium Acetate

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CONTINUING our study of pyrolytic reactions and mechanisms,[1–3] including pyrosynthesis of carcinogenic hydrocarbons,[4–6] we pyrolysed acetic acid, as the sodium salt, at various temperatures and noted the formation of a number of products not formerly found.[7] These products, in addition to polynuclear aromatic hydrocarbons, consisted of 3,5-dimethylphenol, mesitylene, isophorone, mesityl oxide and others which perhaps, in retrospect, should not have been entirely unexpected in view of feasible fragmentation patterns for sodium acetate.

Pyrolyses were effected at temperatures ranging from 500—800° following introduction of pyrolysand (1 g.) into a preheated horizontal quartz tube (4 ft. × 1·25 in. o.d.) packed with quartz chips and continually flushed with nitrogen (30 ml./min.). Residence times of pyrolysand in the reaction chamber were estimated to range between 10 and 30 sec., depending on temperature. Condensable products were collected in traps cooled with Dry Ice–acetone, and following fractionation into acids and neutrals were analysed by g.l.p.c. Identification of products was based on retention, co-chromatographic and spectral (u.v., i.r., and/or mass) data. Relative yields were determined by measuring (by triangulation) chromatographic peak areas.

Products identified, and their relative abundance as a function of pyrolytic temperature are tabulated below. At 500°, mesityl oxide (I), mesitylene (II), isophorone (III), and 3,5-dimethylphenol (IV) predominate. At 600°, the yield of (IV) is substantially increased with corresponding loss in mesityl oxide and isophorone. At 700°, the latter two compounds are absent, (IV) is reduced in yield, and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *m*-xylene, styrene, and naphthalene begin to appear in quantity. At 800°, (IV) is no longer a major constituent in the pyrolysate, whereas the level of naphthalene is substantially increased, and other polynuclear aromatic hydrocarbons such as anthracene, pyrene, and benzo[*a*]pyrene[4,8] occur. At the higher temperatures, as expected, the pyrolysates become more complex and increasingly aromatic (Table).

In trying to rationalize the formation of some of the above products from sodium acetate, we noted that, among them, mesityl oxide and isophorone are known aldol condensation products of acetone. Similarly, trimerization of acetone, followed by dehydration, is known to yield mesitylene.[9] It would seem, therefore, that formation of acetone (*e.g.* from two molecules of sodium acetate) and its subsequent self-condensation might be significant steps in the pyrolytic pathway from sodium acetate to products. Pyrolytic production of acetone was verified by passing the gaseous effluent from the reaction chamber through a solution of 2,4-dinitrophenylhydrazine and isolating the expected hydrazone of acetone. Secondary pyrolysis of isophorone (the latter from 3 moles of acetone) accompanied by loss of methane and tautomerization could lead to (IV) which, in turn could fragment further (via loss of methyl radicals) to *m*-cresol and phenol (Figure). By similar processes, mesitylene could form other alkyl benzenes (toluene, xylene), and possibly polynuclear aromatic hydrocarbons. Some basis for the foregoing pathways is provided by two industrial processes, one of which utilizes acetone[10] and the other isophorone[11] for the thermal production of 3,5-dimethylphenol.

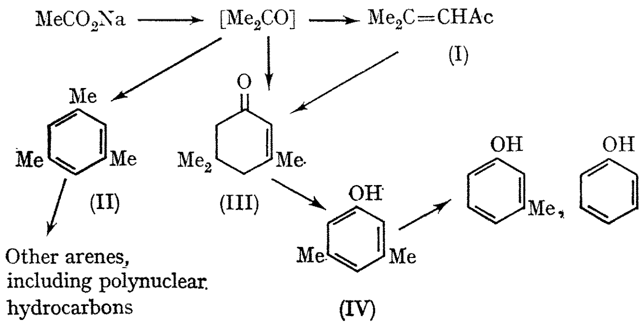

FIGURE. *Suggested pyrolytic pathway*

*Products from sodium acetate pyrolysis* ($N_2$)
*Product distribution* (*per cent.*)[a]

| Products[b] | 500° | 600° | 700° | 800° |
|---|---|---|---|---|
| Benzene | | 3 | 14 | 13 |
| Toluene | | 2 | 11 | 16 |
| Mesityl oxide | 26 | 15 | | |
| Xylenes[c] | | | 14 | 7 |
| Ethylbenzene | | | | |
| Styrene | | 3 | 8 | 10 |
| Mesitylene | 9 | 13 | 7 | |
| Isophorone | 18 | 4 | | |
| 3,5-Dimethylphenol[d] | 14 | 36 | 16 | 5 |
| Naphthalene | | | 6 | 16 |
| Others[e] | 33 | 24 | 24 | 33 |
| Aromatic hydrocarbons | 9 | 23 | 71 | 90 |
| Other aromatics | 18 | 41 | 25 | 10 |
| Non-aromatics | 73 | 36 | 3 | |

[a] Values are based on g.l.p.c. peak areas (in comparable chromatograms) adjusted to an attenuation of 1. [b] In order of elution time (in g.l.p.c.). [c] Mixture of *m*- and *p*-xylene, predominantly *m*-xylene. [d] In a typical pyrolysis (600°), 218 mg. of 3,5-dimethylphenol were obtained per 100 g. starting material ($CH_3CO_2Na{\cdot}3H_2O$). [e] Minor products identified (at various temperatures) include *p*-methylstyrene, indene, phenol, *m*-cresol, trimethylphenols, alkylnaphthalenes, acenaphthylene, fluorene, anthracene, phenanthrene, pyrene and benzo[*a*]pyrene.

Although pyrolysis of sodium acetate resulted in a variety of products, sodium formate yielded no condensable materials at all.

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[1] I. Schmeltz and W. S. Schlotzhauer, *Nature*, 1968, **219**, 370.
[2] T. C. Jones and I. Schmeltz, *Chem. and Ind.*, 1968, 1480.
[3] T. C. Jones and I. Schmeltz, *J. Org. Chem.*, in the press; see also *Chem. Eng. News*, 1968, **46** (12), 38.
[4] W. S. Schlotzhauer and I. Schmeltz, *Beiträge z. Tabakforschung*, 1968, **4**, 176.
[5] J. A. S. Gilbert and A. J. Lindsey, *Brit. J. Cancer*, 1957, **11**, 398.
[6] E. L. Wynder and D. Hoffmann, *Science*, 1968, **162**, 862.
[7] C. D. Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929.
[8] I. Schmeltz, R. L. Stedman, and W. J. Chamberlain, *Analyt. Chem.*, 1964, **36**, 2499.
[9] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, 1961, pp. 458, 647.
[10] T. Mazume, S. Yamada, and K. Abe, Jap.P. 181,443/1950 (*Chem. Abs.*, 1952, **46** 4028e).
[11] P. H. Williams, S. A. Ballard, and T. W. Evans, B.P. 584,256/1947 (*Chem. Abs.*, 1947, **41**, 6899d).