# *A Tracer Study on the Source of Carbon Dioxide in the Chromic Acid Oxidation of Toluene and Fluorene*

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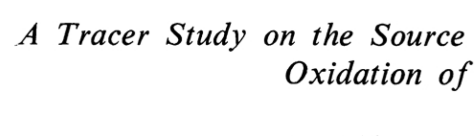
In our previous reports[1,2] it has been found that the chromic acid oxidation of toluenes or fluorene in acetic acid gave carbon dioxide, together with benzoic acids or fluorenone respectively. The following mechanism was suggested to explain the second-order rate with chromium trioxide and the evolution of carbon dioxide:



$$C_6H_5CH_3 + 2CrO_3 \rightarrow C_6H_5CH\left\langle\begin{matrix} O\text{-}\overset{\overset{O}{\|}}{Cr}\text{-}OH \\ O\text{-}\underset{\underset{O}{\|}}{Cr}\text{-}OH\end{matrix}\right. \xrightarrow{2CrO_3} C_6H_5COOH + 2Cr_2O_3 + H_2O + 3O \quad (1)$$

In order to get more information on the source of carbon dioxide, the oxidations to toluene and fluorene were carried out under conditions similar to those described in the previous reports, using labeled acetic acid as the solvent. The liberated carbon dioxide was taken out as barium carbonate, and the radioactivity estimated. The radioactivity of only 18 cpm in barium carbonate obtained from the oxidation of toluene (No. 1 in Table I) shows that the carbon dioxide derived from the oxidation of acetic acid is only 2.5% ($18\times100/716$) of the total carbon dioxide evolved, where 716 cpm is the radioactivity of the solvent acetic acid. The values for fluorene (Nos. 4 and 5 in Table I) show that 1.7∼2.8% of carbon dioxide is derived from acetic acid. Benzoic acid was found to be stable under the experimental conditions (No. 3 in Table I).

If the side chain of toluene is attacked, the reaction products should contain benzene, phenols, quinones and/or biphenyl. Only *p*-benzoquinone was detected by gas chromatography, however. It was found by visible spectrophotometry that the amount of quinone was very small. It was observed that quinone was easily oxidized to carbon dioxide and water by an acetic acid solution of chromic acid (No. 8 in Table I).

In conclusion, the benzene ring of toluene is probably completely broken by active oxygen to carbon dioxide; i. e., the side chain of toluene and/or benzoic acid is oxidized by the active oxygen produced from Eq. 1 to quinone, and then the quinone is further oxidized by chromic acid to carbon dioxide and water. However, the consumption of the starting material, toluene, by this attack of active oxygen is so small compared with that of chromium trioxide that there is no appreciable influence on the rate equation.

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[1] Y. Ogata, A. Fukui and S. Yuguchi, *J. Am. Chem. Soc.*, **74**, 2707 (1952).

[2] Y. Ogata and H. Akimoto, *J. Org. Chem.*, **27**, 294 (1962).

TABLE I. CHROMIC ACID OXIDATIONS IN ACETIC ACID

Solvent, $CH_3CO_2H$ : 15 ml. for Nos. 1—3 and 8 and 30 ml. for Nos. 4—7;
$CrO_3$ : $4.15\times10^{-3}$ mol. for Nos. 1—3 and $7.29\times10^{-3}$ mol. for Nos. 4—7

| No. | Substrate ($10^{-3}$ mol.) | Temp. °C | Time hr. | Obtained $BaCO_3$ g. | Radioactivity $CH_3CO_2H$ c.p.m. | Radioactivity $BaCO_3$ c.p.m. |
|---|---|---|---|---|---|---|
| 1 | Toluene (0.833) | 70 | 3 | 0.211 | 716 | 18 |
| 2 | None | 70 | 3 | 0.065 | 0 | 0 |
| 3 | Benzoic acid (0.833) | 70 | 3 | 0.080 | 0 | 0 |
| 4 | Fluorene (2.43) | 40 | 2 | 0.218 | 358 | 10 |
| 5 | Fluprene (2.43) | 40 | 2 | 0.201 | 358 | 6 |
| 6 | None | 40 | 2 | 0.008 | 0 | 0 |
| 7 | Fluorenone (2.43) | 40 | 2 | 0.276 | 0 | 0 |
| 8 | *p*-Benzoquinone (0.833) | 70 | 3 | 0.682 | 0 | 0 |

Similar results were obtained in the tracer study of the chromic acid oxidation of fluorene in acetic acid-1-$^{14}C$ (Nos. 4 and 5 in Table I); this indicates that the aromatic ring is completely broken by active oxygen to produce carbon dioxide.

## Experimental

**Materials.**—All the materials were purified as in the previous papers.[1,2] Acetic acid-1-$^{14}C$ was synthesized from labeled barium carbonate via the reaction with methyl magnesium iodide.[3] The radioactivity of all the radioactive materials were measured by a Geiger-Müller counter after their conversion to barium carbonate. The radioactivities of barium carbonate were measured by using layers of infinite thickness and corrected for their background.

**Oxidation.** — The carbon dioxide evolved was swept out by passing oxygen-free dry nitrogen gas through and then absorbed by aqueous barium hydroxide after passing it through aniline to eliminate the acetic acid.

**The Gas Chromatography of the Oxidation Products.**—The solution of the reaction product was added to sodium bicarbonate to neutralize acetic acid and benzoic acid and then extracted with ethyl ether. The extract was dried and analyzed by gas chromatography on a 1.5 m. copper column packed with Silicon DC 703 at a helium pressure of 21 p. s. i. at 70°C (for benzene), at 100°C (for quinone), at 170°C (for phenol) or at 190°C (for biphenyl). No indication of the presence of benzene, phenol or biphenyl was observed. *p*-Benzoquinone was identified by having the same peak as the authentic sample and also by color tests with sulfuric acid or sodium hydroxide.[4]

**The Estimation of the Concentration of Quinone.**—The reaction products was extracted with ether, the extract being analyzed spectrophotometrically at the wavelength of the absorption maximum, 430 m$\mu$ with 1 cm. cells. The reaction mixture was found to contain ca. $7\times10^{-3}$ M benzoquinone, which was to be less 1/30 of the calculated concentration ($240\times10^{-3}$ M) on the assumption that one mole of toluene gave one mole each of carbon dioxide and quinone.

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[3] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley & Sons, Inc., New York (1949), p. 175.

[4] R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. XI, Interscience Encyclopaedia Inc., New York (1950), p. 410.