Communications to the Editor

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ELECTRON IMPACT REACTOR FOR ORGANIC REACTIONS

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An electron impact reactor was developed. It permits the isolation of the reaction products induced by accerelated electron beams. The reaction was found by a rate law study to be consistent with rate-limiting, electron impact activation. Some electron impact fragmentation reactions using this apparatus are shown.

KEYWORDS—electron impact; mass spectrometry; anisole; rate law; organic reaction

A number of articles have been presented on the relationship between mass spectrometric (electron impact), thermolytic and photolytic fragmentation reactions,[1-3] but a clear general understanding of this relationship still eludes us. Recently, organic plasmolysis,[4] reactions in the plasma caused by radio frequency discharges, has become available to investigate the nature of the electron impact fragmentation of organic compounds. However, the interpretation of organic mass spectra has been a major approach to solve this problem. We wish to report here a study using a promising technique based on a newly developed electron impact reactor which affords reaction products induced by an accelerated electron beam. With this technique, the detailed mass spectrometric fragmentation paths can be studied directly.

The apparatus for this experiment is shown in Fig. 1. The reactant introduced by sublimation at the right end of the reactor is subjected to excitation by electron impact, then the product is trapped in a liquid nitrogen trap. This whole apparatus is maintained under low pressure (10^{-5} Torr) using a high vacuum pumping system. A Pyrex electron impact reactor is shown in Fig. 2.

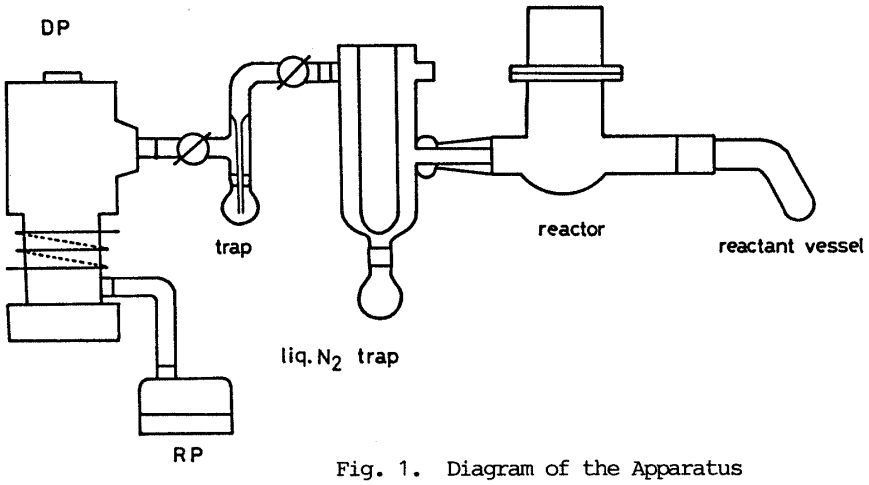

Fig. 1. Diagram of the Apparatus

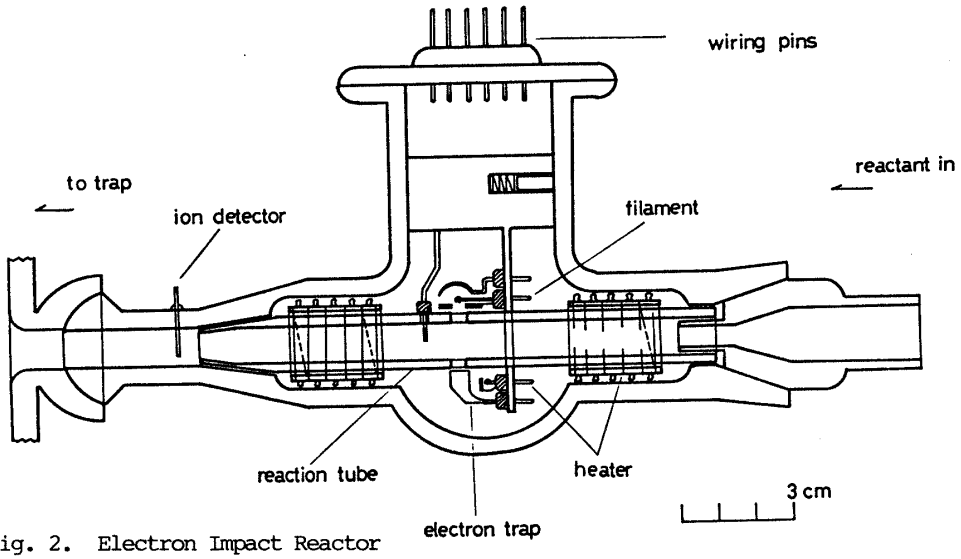

Fig. 2. Electron Impact Reactor

The accelerated electron beam passing across the middle of the reaction tube irradiates the molecular stream of the reactant.

In the first part of this study, the isomerization of anisole, whose isomerization in plasmolysis had already been studied in detail,[5] was examined to compare the nature of the reaction. The electron impact reaction mechanism of anisole in plasmolysis is shown in Fig. 3. In this experiment a result similar to that with plasmolysis is expected if the reaction is based on electron impact activation alone, though other activations, such as thermolytic for instance, are likely to occur because there is a highly heated tungsten filament near the reaction tube. Figure 4 shows the GC/MS ion chromatogram of the reaction mixture and the GC peaks of the three major products, phenol, o-cresol and p-cresol. Moreover, kinetics studies confirmed that the electron impact is the rate-determining step in this reaction. It is

generally accepted that the rate of reaction depends on the electron energy function ($f(\varepsilon)$). From this the following equation can be derived:

$$-\ln(p_1/p_1^0) = k_1\tau f(\varepsilon),$$

where p_1^0 is the pressure of anisole at the entrance to the reactor, p_1 is the anisole pressure at the exit from the reactor, and τ is the residence time in the reactor. Assuming a direct dependence of $f(\varepsilon)$ on P/p (P: power of the filament, p: pressure in the reactor),[5] the following equation can be given:[6]

$$-\ln U = k'\tau P/p,$$

where U is the fraction of anisole recovered and k' includes all the proportionality constants. Considering the observed reactant flow (f),

$$\tau/p = V/RTf$$

follows from the ideal gas law. The least-squares line $-\log U = 0.003P/f+0.057$, shown in the kinetic experiment of anisole (Fig.5), indicates that the electron impact on anisole is the rate-limiting step in this reaction.

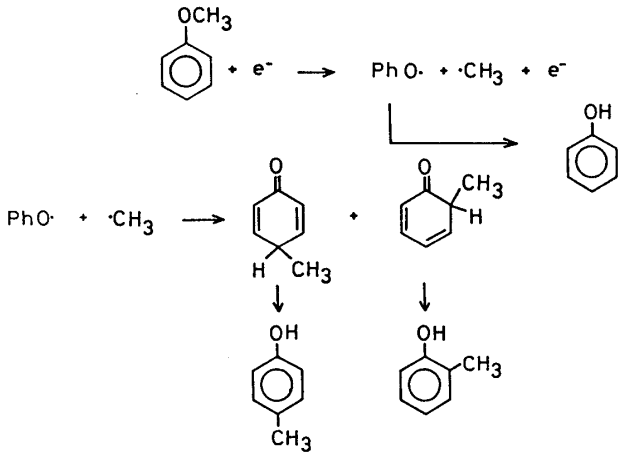

Fig. 3. Electron Impact Reaction of Anisole

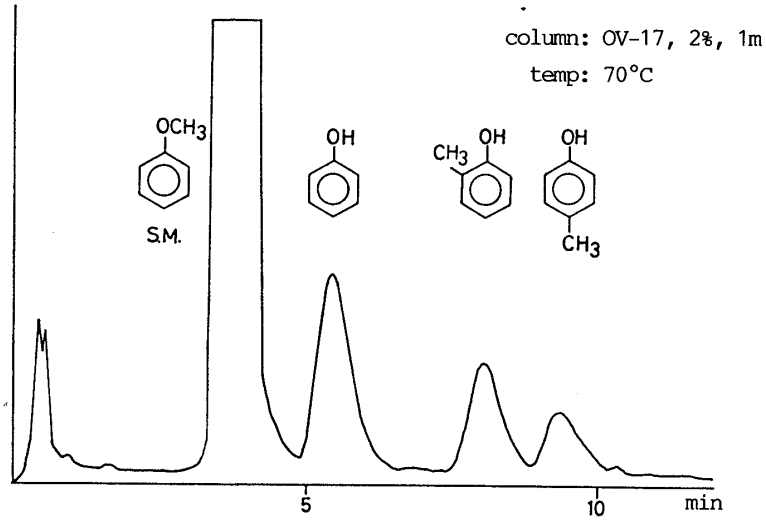

Fig. 4. GC/MS Analysis (RIC,50-300m/z) of Reaction Products

This experimental method was applied to several organic compounds. A typical application was a flow rate of 0.3 mmol/min at 40 W of filament power and 50 V of electron potential, using 700 mg of starting material.

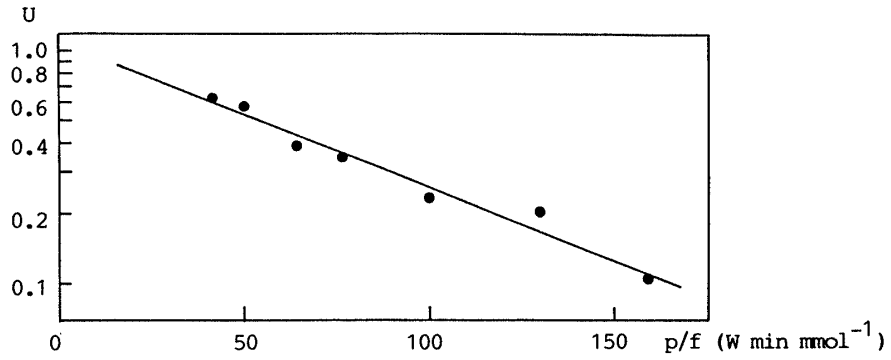

Fig. 5. Kinetics of Anisole

The results of the electron impact fragmentation reactions are shown in Fig. 6. These results indicate that, using this apparatus, reaction products induced by electron impact are available in isolable scale. The elucidation of this reaction mechanism compared to the mass spectrum is a subject of continuing studies.

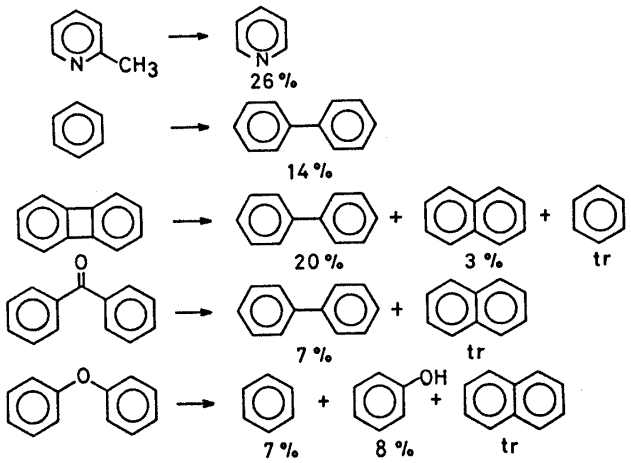

Fig. 6. Electron Impact Reactions

REFERENCES AND NOTES

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6) It was suggested that the electron impact effect depends mainly on the number of the electrons, since very little electron potential dependence was observed in this apparatus.

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