The Electronic Spectrum of Cumene Adsorbed on the Silica-Alumina Catalyst Surface during the Cracking Reaction[*]

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It is generally assumed that cumene dealkylation over silica-alumina catalyst involves, as an intermediate, the protonated cumene formed by the addition of a proton to cumene[1]. However, the existence of this intermediate has not yet been proven, although it is considered to form on the surface of catalyst during cracking. Since chemical species such as hydrocarbon ions or radicals often show a characteristic electronic spectrum, it is interesting, in studying the cracking mechanism, to investigate those species adsorbed on the catalyst by measuring their electronic spectra. Recently such studies have been reported by Leftin and Hall[2a-c], who have demonstrated the formation of dimethylphenyl-carbonium ions in the chemisorption of cumene. However, these ions are inconsistent with the generally accepted mechanism for the dealkylation reaction. It should be noted that Leftin's spectral measurement was carried out at room temperature. In order to detect an unstable intermediate on a catalyst, the spectra should be measured on the catalyst during cracking. Such a study, which will be reported on here, should contribute substantially to establishing the reaction mechanism.

Experimental

Cumene was washed with concentrated sulfuric acid and then dried and distilled. The distillate was percolated through columns of silica gel to remove the peroxide.

The silica-alumina catalyst, which had been prepared by the coprecipitation method and which had been calcinated at 500°C in air for 2 hr., was kindly supplied by Prof. Shiba of the Tokyo Institute of Technology and was said to contain approximately 10% alumina. This catalyst was prepared for optical measurement in the form of a semitransparent thin disk (0.1 mm. thick) by pressing its powder at a pressure of 8 ton./cm^2. This disk was placed in an optical cell similar to that described

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[1] M. F. L. Johnson and J. S. Melik, *J. Phys. Chem.*, **65**, 1146 (1961).

[2] a) H. P. Leftin and W. K. Hall, Proceedings of the 2nd International Congress on Catalysis, Paris, France, July, 1950. b) H. P. Leftin, *J. Phys. Chem.*, **64**, 1714 (1960). c) H. P. Leftin and W. K. Hall, ibid., **66**, 1457 (1962).

previously[3]. Heating was provided by a winding of nichrom wire around the outside of the cell; thus the spectrum during reaction at an elevated temperature was obtained. This cell was connected directly to the vacuum system, evacuated for one hour at 300°C, and then sealed off under vacuum. The pure cumene sample to be adsorbed was sealed in a separate compartment, one separated from the cell by a break-off seal. Exposure of the catalyst disk to cumene vapor was carried out by rupturing this break off seal. Exposure times of several hours were allowed to make an equilibrium condition at room temperature. The optical spectra were measured with a Hitachi EPS-2 recording spectrophotometer and were determined by measuring the transmission through this disk. Another disk, pretreated identically in a separate cell, was used as a blank in the reference beam.

Results and Consideration

At first, the absorption spectrum of the material adsorbed on the catalyst disk was measured at room temperature. As is shown by curve A of Fig. 1, the spectrum obtained is characterized by a double peak absorption band in the 258∼265 mμ region and is almost identical with the spectrum of an alcoholic solution of cumene, indicating that cumene is physically adsorbed on the catalyst.

The cell was then heated to 150°C, and the absorption spectra at this temperature were taken at various intervals of time. The results are shown by curves B–E of Fig. 1. On heating at 150°C for 30 min., a new band appeared at 335 mμ. With further heating, another band appeared at 430 mμ; this finally proved to be the most intense band.

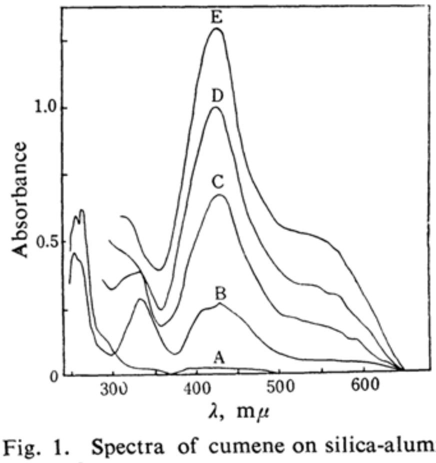

Fig. 1. Spectra of cumene on silica-alumina.
A : Room temperature
B : Heated 150°C for 1 hr.
C : Heated 150°C for 3 hr.
D : Heated 150°C for 6 hr.
E : Heated 150°C for 17 hr.

After heating for 17 hr., the gases in the cell were spectrophotometrically analyzed. The liquid product was mainly benzene, with a small amount of di-isopropylbenzene. This shows that the cracking dealkylation reaction took place mainly in the cell, though the reaction was followed at a lower temperature than that for catalytic cracking in usual (350∼450°C). The 430 and 335 mμ bands were not found with the reaction product. Therefore, the bands at both 430 and 335 mμ are ascribed to chemisorbed molecules formed on the catalyst during the cracking reaction.

Recently, Leftin and Hall[2a] have shown, by spectrophotometric studies, that when triphenylmethane and related compounds, including cumene, are adsorbed on the surface of thoroughly dried silica-alumina catalysts, carbonium ions are formed which have an absorption band at about 400 mμ. With reference to their results, the 430 mμ band indicated by curves B–E of Fig. 1 can be assigned to a stable dimethylphenylcarbonium ion produced between cumene and the Lewis acid site on the silica-alumina surface. After the catalyst had been heated at 150°C for 17 hr., it was exposed to air at room temperature. In this case, the 430 mμ band was still observed, and the catalyst developed a brown color. When the catalyst was treated with an aqueous solution of ammonia, the brown color was lost and the 430 mμ band completely disappeared. This indicates that the carbonium ion is displaced from the acid center by the ammonia molecule, which forms a stronger base.

On the other hand, when the 335 mμ band was superimposed on the absorption in the ultraviolet region, which developed gradually with time, it became quite obscure after 6 hr. By reducing the effect of the absorption of the background at the ultraviolet region, it was found that the absorbance at 355 mμ after one hour is almost the same as that after three hours. In order to investigate in more detail the behavior of this band in relation to the time, measurements were made in an earlier stage of reaction. The results are shown by curves A and B of Fig. 2. It may be seen that, immediately after the temperature of cell reached 150°C, an absorption band appeared 327 mμ and that, thereafter, it increased in absorbance with a shift to 335 mμ. In this period the 430 mμ band had not yet appeared. After 13 min., heating was stopped and the spectrum was measured at room temperature. As is shown by curve C of Fig. 2, the 335 mμ absorption was considerably decreased, though absorbance around this peak increased. This fact indicates that the surface

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[3] M. Okuda, *J. Chem. Soc. Japan, Pure Chem Sec.* (*Nippon Kagaku Zasshi*), **82**, 1115 (1961).

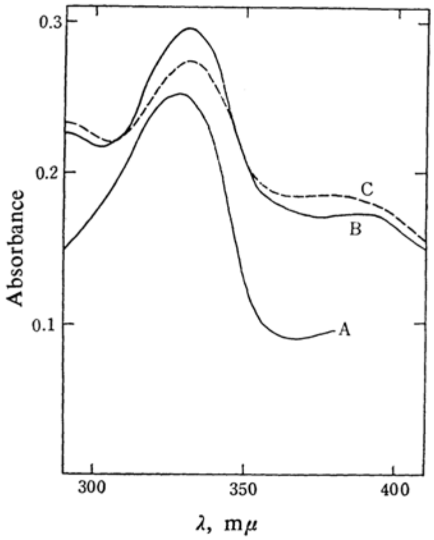

Fig. 2. Spectra of cumene on silica-alumina.
A : Immediately after heating at 150°C
B : Heated 150°C for 13 min.
C : At room temperature after heating for 13 min.

species contributing to the formation of this band ceased to be formed at room temperature.

On the basis of these results, it is suggested that the 335 mμ band could be due to an intermediate in the cracking reaction. A similar spectrum, with a peak at 327.5 mμ, was obtained from a solution of cumene in concentrated sulfuric acid. This absorption disappeared after 20 hr.; therefore, it is due to an unstable chemical species, probably protonated cumene, since it is well known that such hydrocarbon acts as a base in concentrated sulfuric acid and forms a proton adduct⁴⁾. It seems probable that the unstable intermediate on the catalyst is also a protonated cumene produced by the reaction of cumene with the Brönsted acid site of the catalyst.

In summary, under the experimental conditions used, there exist both a Lewis acid site and a Brönsted acid site on the surface of the silica-alumina catalyst; the latter contributes to the cracking reaction through the formation of a chemisorbed intermediate.

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4) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, **1936**, 1637.