proper conditions, the primary step (1) can be isolated for all the primary aliphatic alcohols on $\gamma - Al_2O_3$. This step is bimolecular and since the reaction order $n = 0$ can be found, presumably is a Langmuir-Hinshelwood mechanism.

The olefins, formed either in a primary step according to (2) or in secondary steps according to (3) and (4), always have the double bond in the end position. These products can then isomerize further. Skeletal isomerization takes place only to a small extent.

Branched aliphatic alcohols. From the values of the free reaction enthalpies, it can be shown that the ether formation from these alcohols is thermodynamically less favorable than for the unbranched alcohols. In fact, a small ether concentration can be proved only for isopropanol, while simultaneously olefin is formed directly. From isobutanol and tertiary butanol the only product is isobutylene. The dehydration of secondary butanol gives, in apparently parallel steps, 1-butene, as well as *cis*- and *trans*-2-butene. The formation of the *cis* product is here greatly preferred.

If the "principle of least motion" is valid, then, because of the comparable product distribution, a comparison with regard to the mechanism of similar reaction stages for the various alcohols may be concluded, with a certain degree of probability, even without an exact knowledge of the actual reaction mechanism and the elementary steps.

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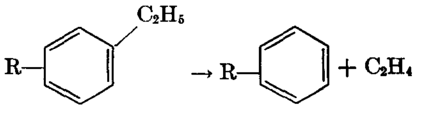
Correlation of Reactivity and Adsorptivity of Ethylbenzene and Ethyltoluenes

The gas chromatographic method allows study of the adsorption of substrates on solid catalysts at actual reaction conditions (*1–4*). One of the points of interest in conducting these measurements is the comparison of adsorptivity and reactivity of isomeric or homologous compounds, i.e. the comparison of structure effects on adsorption properties and reaction ability.

In studying the transformations of ethylbenzene and three isomeric ethyltoluenes on an acidic catalyst (*5*) we have obtained good correlation between dealkylation rates and retention times. The catalyst which was prepared by impregnation of alumina with an aluminum fluoroborate solution (*6*) has catalytic properties in many respects similar to silica-alumina (*7*). The rate of dealkylation [Eq. (1)] was determined at 400°C



(1)

R = H, o-CH_3, m-CH_3, p-CH_3

in a flow integral reactor with hydrogen as diluent and the rate constants were estimated by means of a Langmuir-Hinshelwood–type rate equation. The adsorption of the substrates was measured by the pulse-flow technique in a standard gas chromatographic apparatus with a thermal conductivity cell. Hydrogen was used as the carrier gas and the size of the samples was 2 μl. The heats of adsorption were estimated by the method of Eberly (*3*) from the retention data obtained at various temperatures.

TABLE 1
RATE CONSTANTS, RETENTION TIMES, AND HEATS OF ADSORPTION

Compound	Rate constant (mole/hr kg)	Retention time (sec)	Heat of adsorption (kcal/mole)
Ethylbenzene	0.23	86	5.9
o-Ethyltoluene	12.62	179	6.0
m-Ethyltoluene	5.52	142	7.3
p-Ethyltoluene	11.71	166	6.2

In Table 1 the specific reaction rate values, the retention times, and the heats of adsorption are summarized. A parallelism between the changes of the values of these constants with the change of the structure of the substances may be observed.

We suppose that observed effects of structure have a common cause in different basicities of the hydrocarbons. In order to check this hypothesis the values for xylenes for 25°C (*8*) may be used, under the assumption that the relative basicities in the series ethylbenzene, *o*-, *m*-, and *p*-ethyltoluenes are practically the same as in the series toluene, *o*-, *m*-, and *p*-xylenes. Taking both the retention times and the heats of adsorption, extrapolating the retention data to 25°C, and comparing them with values published by Brown and Brady (*8*), a good agreement with relative σ basicities is obtained. In contrast, Mosely and Archibald (*4*) have found no correlation of retention volumes of isomeric xylenes on silica-alumina at 280° and 350°C with σ and π basicities; however, these authors have not taken into account the possible differences in the heats of adsorption, i.e. the change of basicities with temperature.

In Fig. 1 the relative rate constants for dealkylation and the relative retention times are correlated. The log–log plot applied here is analogous to linear free energy relationships which are used in theoretical organic chemistry for correlating structure effects on rates or equilibria (*9*). According to expectation, the point for *o*-ethyltoluene shows a deviation from linearity. The correlation coefficient for ethylbenzene, *m*-ethyltoluene, and *p*-ethyltoluene values was calculated as 0.999.

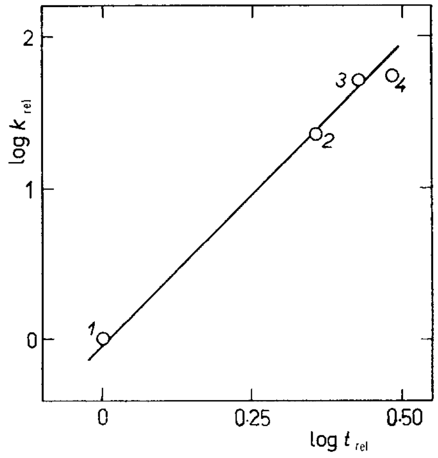


FIG. 1. Correlation of relative rate constants of dealkylation and relative retention times (corrected for different volatility). 1, Ethylbenzene; 2, *m*-ethyltoluene; 3, *p*-ethyltoluene; 4, *o*-ethyltoluene.

The successful correlation of σ basicities, retention times, and reactivities indicates that in our case a σ complex is very probably formed on the surface of the catalyst in the adsorption step and that this complex is an intermediate in the dealkylation.

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The Activity of Abraded Copper/Copper Oxide Foils in Heterogeneous Catalysis

It has been claimed (*1, 2*) in recent years that the activity of metal oxides in heterogeneous catalytic reactions may be understood better by applying the newer theories of inorganic complex formation to those processes occurring at a surface. This is in contrast to relating activity patterns to properties of oxides as semiconductors in terms of the band theory of solids (*3*). In both of these approaches, however, attention has to be given to the chemical and mechanical nature of the surface. In particular, the influence of Volkenshtein's micro- and macroscopic defects (*4*) have to be considered.

In this investigation the activity of "Specpure" copper foils (6 cm × 3 cm × 0.1 mm thick), initially supporting air-grown oxide films, was examined in the decomposition of hydrogen peroxide vapor. A comparison was sought for the performance of cuprous oxide films supported on (a) smooth and (b) abraded copper surfaces. The flow apparatus, metal foil reactor and experimental technique adopted have been described previously (*5*). The steady activity level was determined at each point in the temperature cycle 80°–60°–100°–40°. Abrasions were introduced by scratching the foils carefully with a sharp corner of the same material along a straight edge. Prior to exposure to H_2O_2 vapor both smooth and abraded foils were annealed in air for 45 min at 80°.

Figure 1 shows the variation of activity (as percentage decomposition) with time in achieving the steady level. In general smooth foils attained this level after 40 min exposure. At 100°, the initial fall and then rise in activity of the lower temperatures was not detected. This is consistent with earlier findings using "Specpure" slips (*5*), and may be connected with the growth of an oxide film on the metal.

The effect of abrasion on activity is shown also in Fig. 1, for foils scratched 6 cm in length and ca. 0.1 mm in width along two diagonals. A surprising increase in activity was detected, most pronounced at the lower temperatures. On first exposure to H_2O_2 vapor some cyclic activity variation was noted and the first steady level at 80° was not achieved before 90–100 min exposure. Subsequent runs settled to the same steady level in 40 min, and no deterioration in activity was detected after standing the foils in air at room temperature for three days.

Foils were abraded further by 3 parallel scratches, 6 cm long spaced 0.5 cm, crossing the diagonals. Little or no further improvement was detected with these specimens. Thus at 80°, diagonally abraded foils gave 87% decomposition which increased only to 88.6% on further treatment.

In Fig. 2, Arrhenius plots of first order rate constants are shown for (a) smooth and (b) abraded foils. These plots gave