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LASER PYROLYSIS GAS CHROMATOGRAPHY OF SEVERAL AROMATIC CARBOXYLIC ACIDS. EFFECT OF ADDITION OF SODIUM BOROHYDRIDE

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Aromatic carboxylic acids mixed with sodium borohydride ($NaBH_4$) were degraded by a defocused laser beam in the normal pulse mode. The addition of $NaBH_4$ resulted in significant increases in the yields of decarboxylated products and the pyrograms obtained provided useful information about the structures of parent compounds.

In the previous papers1)-4) the authors described laser pyrolysis gas chromatography (LPGC) of several types of aliphatic compounds and discussed the correlation between the molecular structures of sample compounds and the distribution of products. The work reported here is the application of this technique to aromatic carboxylic acids.

The LPGC system used was the same as described in the previous papers.1)2) Briefly, a sample coated on the sample holder was placed in the pyrolysis tube connected to the gas chromatographic column and irradiated with a laser beam. The sample compound was mixed with 5 % powdered carbon. The ruby laser was operated at 0.5-joule laser output in the normal pulse mode. The gas chromatographic conditions were as follows:

Column: 2-m by 3-mm i. d. column packed with 9 % Apiezon grease L on 80/100 mesh Gas Chrom Q.
Column temperature: 150 °C.
Carrier gas: nitrogen 15 ml/min.
Detector: FID.

Products were identified by comparison of their retention values with those of known compounds and/or by using a Hitachi RM-50GC gas chromatograph - mass spectrometer.

In the laser-induced degradation of salts of aliphatic carboxylic acids, most products were formed by decarboxylation followed by the unimolecular decomposition of free radicals such as β-scission, as described previously.2) The distribution of these products were closely related to the carbon skeletons of parent compounds. Only slight amounts of longer-chain paraffins were formed by the abstraction of hydrogen.

At the beginning of this work, aromatic acids mixed with powdered carbon alone were degraded by a defocused laser beam. The degradation of aromatic acids gives low molecular weight products and benzene derivatives. The former products consist of large amounts of acetylene, methane and ethylene and have been formed by the unimolecular decomposition of initial radicals formed by decarboxylation. These products are not useful for the elucidation of the molecular structures of aromatic acids. The latter products are produced by bimolecular processes such as the abstraction of hydrogen by aryl radicals formed by decarboxylation. Consider the heats of reaction for the following reaction processes as typical examples in order to compare the pyrolyses of aromatic acids with those of salts of aliphatic acids:

$$nC_6\cdot \longrightarrow 3\ CH_2{=}CH_2 + H\cdot \qquad \text{----------} \ (1)$$

$$Ph\cdot \longrightarrow 2\ CH{\equiv}CH + CH{\equiv}C\cdot \qquad \text{----------} \ (2)$$

A large amount of ethylene is obtained in the degradation of a salt of heptanoic acid and it is thought that a considerable part of this product must be formed by process (1). Process (1) consists of three consecutive β-scissions. The heat of reaction for each step is estimated to be 20 to 40 kcal/mol and the total heat of reaction for process (1) is estimated to be about 80 kcal/mol. On the other hand, the total heat of reaction for process (2) is estimated to be about 160 kcal/mol. These values were calculated using standard heats of formation of radicals estimated by the method of Kagiya et al.[5] Thus, the unimolecular decomposition of aryl radicals would be much more endothermic reaction than that of alkyl radicals and so aryl radicals would have relatively longer life time. Therefore, it is expected that the products of bimolecular processes are obtained in considerable amounts in the degradation of aromatic acids.

In order to obtain pyrograms closely related to the parent structure, it is necessary to fix and stabilize the initial fragments rapidly. For example, it may be suitable for this purpose to degrade sample compounds in the presence of free radical catcher such as NO or I_2. But these species possibly contaminate the gas chromatographic path and are not handled easily. If sample compounds are degraded in the presence of hydrogen donors such as metal hydrides, initial free radicals will probably be fixed and stabilized by catching the hydrogen generated from the hydrogen donors and it is expected that the products formed in such a process reflect the parent structures clearly. So we tried to pyrolyze the sample compounds mixed with sodium borohydride ($NaBH_4$) as a hydrogen donor, which is easy to handle. Figure 1 shows the degradation patterns of several aromatic carboxylic acids. The top of each pair of pyrograms shows results from the degradation of the sample compounds mixed with powdered carbon alone (1a, 2a, 3a, 4a, 5a and 6a). The bottom shows the degradation patterns resulting from the addition of $NaBH_4$ together with carbon (1b, 2b, 3b, 4b, 5b and 6b). It has clearly shown that the addition of $NaBH_4$ results in a significant increase in the yield of decarboxylated products, e. g., benzene, toluene and cumene from benzoic, p-toluic and p-isopropylbenzoic acids, respectively. These products retain characteristics of the parent structures and seem to be as useful as the molecular ion in mass spectrometry. On the other hand, the yield of low molecular weight products is decreased by the addition of $NaBH_4$.

Carboxylic acids containing functional groups other than alkyl groups on the

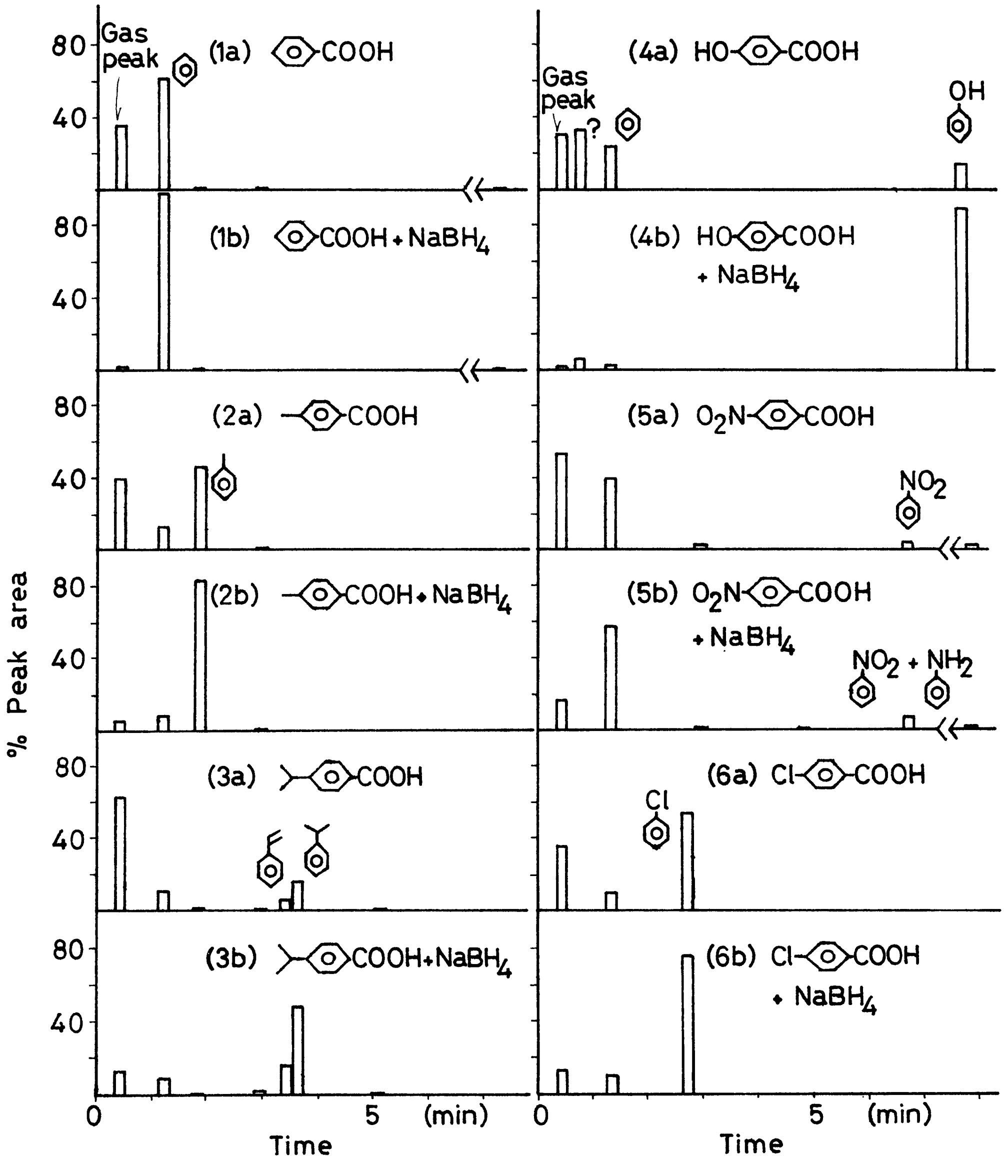

Figure 1. Degradation patterns of aromatic carboxylic acids. Laser output: 0.5 joule; (a)----- Acid: 95 wt%, carbon: 5 wt%; (b)----- Acid + $NaBH_4$ (Acid/$NaBH_4$: 1 mole/mole): 95 wt%, carbon: 5 wt%.

benzene ring were also degraded in the presence of $NaBH_4$. The similar effect is observed in the degradation of p-hydroxy- and p-chlorobenzoic acids and the yields of phenol and chlorobenzene, respectively, are increased. But some substituents may be reduced by $NaBH_4$. For example, when p-nitrobenzoic acid is degraded, aniline is produced together with nitrobenzene.

As described above, the addition of $NaBH_4$ contributes apparently to the stabilization of aryl radicals. It is expected that the similar results will be also obtained in the laser pyrolysis of other aromatic compounds in the presence of $NaBH_4$. Lithium aluminum hydride ($LiAlH_4$) has also the similar effect and the addition of a smaller amount of this hydride is more effective. Degradation patterns of salts of aliphatic carboxylic acids are little affected by the addition of $NaBH_4$, perhaps because alkyl radicals easily decompose unimolecularly. Further detailed investigations are in progress to clarify the degradation mechanism of a compound in the presence of $NaBH_4$ or $LiAlH_4$.

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