FREE PHENYL RADICALS IN THE GAS PHASE

Sir:

In the past few years a number of investigators have demonstrated the existence of active gaseous hydrocarbon molecules in experiments in which various types of substances were thermally decomposed. These have been called free radicals. So far only the methyl and ethyl radicals have been reported. In some experiments which we have been performing we have strong indications of the existence of the free phenyl radical in the gas phase.

The apparatus was made of quartz and consisted of a chamber to contain the lead tetraphenyl, a short region inside an electric furnace inclined slightly from the horizontal, a chamber to retain the liquid and crystalline products formed (chiefly diphenyl) and a chamber in which mercury was kept refluxing. The procedure was similar to that used in our work on the chemical reactions of gaseous methyl and ethyl [THIS JOURNAL, **55,** 2696 (1933)]. The lead tetraphenyl was kept just below its melting point (215–220°) and the apparatus run for six hours at an indicated pressure of 0.01 mm.

The deposit formed in the mercury reflux chamber was recrystallized from alcohol. Among the characteristic broad crystals of diphenyl there appeared scattered needle-like crystals. Several were picked out and an attempt made to determine their melting point. This was in the region of 120° as near as could be determined with this small sample. The melting point of mercury diphenyl is 120°. A qualitative analysis showed mercury.

As neither lead tetraphenyl nor diphenyl reacts with mercury vapor, we believe that active phenyl radicals were present. Further work is in progress on this problem.

DEPARTMENT OF CHEMISTRY
DEPAUL UNIVERSITY, CHICAGO
M. F. DULL
J. H. SIMONS

RECEIVED AUGUST 16, 1933 PUBLISHED SEPTEMBER 5, 1933

THE FORMATION OF FREE RADICALS FROM ALIPHATIC AZO COMPOUNDS

Sir:

In view of the publication of a communication on this subject by Leermakers [THIS JOURNAL, **55,** 3499 (1933)] it seems desirable to publish an account of some work we performed in this connection in August, 1931. We found that both azomethane and azoisopropane readily remove antimony mirrors when passed through a furnace heated in the range 450–550°; acetone was used as the carrier gas. The temperature of the furnace was far too low to cause any perceptible decomposition of the acetone.

At that time we were more particularly interested in azoisopropane because it seemed to offer the possibility of preparing the free isopropyl group. Paneth and his co-workers [*Ber.*, **62,** 1335 (1929); **64,** 2702, 2708 (1931)] had already prepared free methyl and ethyl but had failed to obtain the *n*-propyl or the isobutyl radicals from the corresponding lead compounds; they concluded that a large proportion of the *n*-propyl and isobutyl radicals must have decomposed into methyl groups since zinc dimethyl was identified among the products. It occurred to us, however, that the isopropyl and tertiary butyl radicals should have about the same stability as the ethyl radical, since in all three cases a C–H bond must break in order for the radical to decompose with production of an olefin hydrocarbon, whereas all other paraffin radicals can undergo this decomposition by rupture of a C–C bond. This may be easily seen from the examples given in a previous paper [Rice, THIS JOURNAL, **55,** 3036 (1933)].

We first made some measurements of the rate of disappearance of the active fragments according to the method described by Rice, Johnston and Evering [THIS JOURNAL, **54,** 3529 (1932)]. The following table gives the results obtained with a 1% solution of azoisopropane in acetone, using a quartz tube 0.4 cm. in diameter and an acetone pressure at the standard mirror of 0.22 mm. of mercury; the fall in pressure down the tube was 0.007 mm. per cu.

d, cm.	15	22	11	30	25	18	13	28	20	30	24
t_m, sec.	51	118	33	225	275	71	42	275	83	305	270

d is the distance from the furnace to the standard mirror and t_m is the time of removal of the standard mirror. These results were plotted and compared with the curve obtained for lead tetramethyl under identical conditions. The first parts of the two curves coincide exactly, but at distances greater than 20 cm. from the furnace the concentration of active fragments does not fall off as rapidly in the case of azoisopropane as in the experiments with lead tetramethyl. This behavior would seem to indicate the formation of a fragment of comparatively long life during the decomposition of azoïsopropane. However, at that time we had not yet developed any convenient method of identification and therefore could not determine conclusively whether the isopropyl group was formed, perhaps undergoing partial decomposition into propylene and atomic hydrogen.

JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
F. O. RICE
B. L. EVERING

RECEIVED AUGUST 19, 1933 PUBLISHED SEPTEMBER 5, 1933

INDIUM AND SCANDIUM IN PEGMATITE

Sir:

Indium and scandium have been found in a pegmatite dyke in Western Utah. Analyses of samples taken at random along the dyke indicate 1.0–2.8% indium and 0.5–1.2% scandium.