Radiolysis of CF4–C6H6 Systems

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ments for CO are endowed with greater experimental uncertainties than for N_2, it is clear that in several respects the adsorption behavior of the two gases is different. For the low-temperature α peak this has already been reported[1]; further flash filament experiments reveal that CO also differs in that an additional γ peak is *not* found when adsorption is carried out at 115°K. Furthermore, in the field emission microscope the course of the adsorption of CO on tungsten appears qualitatively the same at temperatures from 80°–350°K, resulting in an increase of the work function ϕ from 4.5 to 5.2 v at saturation at 80°K and $1 \cdot 10^{-8}$ mm. This confirms the absence of an additional low-temperature state analogous to the γ state of N_2. That CO, unlike N_2, does *not* dissociate on the surface is also indicated by both flash filament and field emission observations. In the former, the adsorption of nitrogen has been measured on a tungsten filament, both before and after measurements with CO on the same sample, and has been found unchanged. The behavior of N_2 is sensitive to carbon contamination, and the reproducibility of our measurements therefore indicates the absence of such carbon formation. The field emission patterns for CO on tungsten, moreover, are distinct from those arising from carbon contaminated points and even upon heating to 2300°K at a CO pressure of 2×10^{-8} mm such patterns have not been observed.

Though both the strongly and weakly bound states of chemisorbed N_2 and CO are different in origin, the kinetics of formation of the β states are qualitatively similar. The γ state is unique with nitrogen, however, and we conclude that it therefore should not play a dominant role in the kinetics of formation of the β state—a conclusion supported by detailed kinetic measurements to be reported elsewhere.

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Radiolysis of $CF_4 - C_6H_6$ Systems*

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DURING our studies of the radiation chemistry of halogenated organic compounds, we have observed a series of radiation induced "cross-halogenations" exemplified by the over-all reactions:

$$C_6H_6 + CF_4 \rightarrow C_6H_5CF_3 + HF \tag{1}$$

and

$$C_6H_6 + CF_4 \rightarrow C_6H_5F + CHF_3. \tag{2}$$
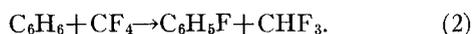
Although reactions similar to (1) and (2) are expected to be generally applicable to many halogen compounds, we have emphasized the $CF_4 - C_6H_6$ system because of (a) the interesting radiation chemistry of the very strong carbon-fluorine bond, (b) the need of obtaining radiation chemical data of fluorinated organic compounds in general, and (c) the desirability of developing a new synthetic method for organic fluorine compounds.
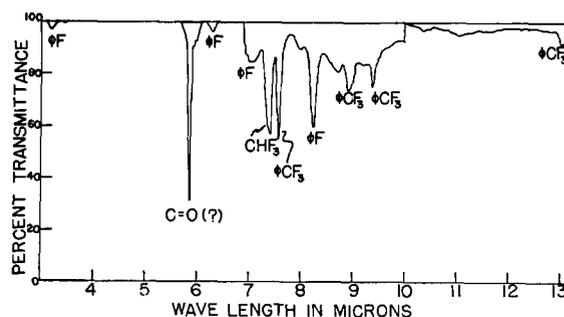

FIG. 1. Infrared spectra of irradiate mixture.

In addition, our experimental results also suggested that, at least for the $CF_4 - C_6H_6$ system, mechanisms other than those of a free radical nature must be responsible for the observed radiation induced reaction.

The experimental work reported herein was carried out with Mallinckrodt AR benzene and Dupont freon-14 (CF_4). Other systems studied included C_6H_6 or $C_6H_5CH_3$ irradiated together with CHF_3, CCl_2F_2, CCl_3F, or $C_2Cl_2F_4$.

The irradiation samples were prepared in the following manner. Known amounts of benzene were introduced to weighed glass irradiation capsules, and were degassed by freezing in liquid nitrogen and evacuation. Predetermined amounts of CF_4 were introduced and the capsules were sealed and reweighed to check the exact amount of reagents introduced. The filled capsules were then irradiated with gamma rays from the Argonne spent fuel facility,[1] a cobalt-60 source, or the Armour reactor fission gas source. After irradiation, the liquid portions of the samples were analyzed directly by a Perkin-Elmer Model 21 double beam infrared spectrophotometer.

Examination of the infrared spectra revealed the formation of $C_6H_5CF_3$, C_6H_5F, and CHF_3 as would be expected from Eqs. (1) and (2). The formation of the other expected product, hydrogen fluoride, was indicated by the attack on the walls of the capsules. An example of the infrared spectra of an irradiated system is shown in Fig. 1, and a plot of the yield of $C_6H_5CF_3$ and C_6H_5F as a function of the over-all CF_4 to C_6H_6 ratio is shown in Fig. 2. In these cases, the yields (G values) were expressed in terms of the number of molecules produced per 100 ev of radiation energy absorbed by the whole mixture, and were determined from the absorption spectra by comparison with standard samples and by application of Beer's law. The
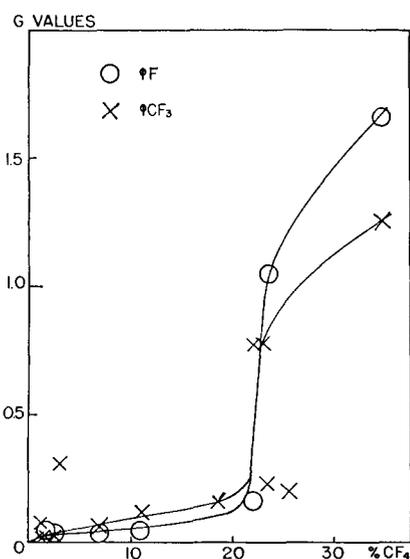
FIG. 2. Yield of C_6H_5F and $C_6H_5CF_3$ as a function of CF_4/C_6H_6.

radiation dosages needed for the yield calculations were based on the ferrous sulfate dosimeter with $G=15.6$.[2]

In separate experiments, we have established that as a first approximation, and under the conditions of our experiment, CF_4 dissolves in benzene in accordance with Henry's law, and that the G(radical) values of $CF_4-C_6H_6$ systems are of the order of 0.7–1.1 as determined by the diphenyl picryl hydrazyl (dpph) method.[3] Since only a fraction of the radiation produced radicals can combine to form the fluorinated aromatic compounds as a result of competition of other combination processes and since the dpph method normally gives higher G(radical) values than those obtained by other methods,[4] it follows that radical combination reactions cannot be responsible for the observed results. This conclusion, coupled with the knowledge that radical-molecule reactions involving F or CF_3 and C_6H_6 lead at best to addition instead of substitution[5] and that CF_4 is immune toward attack by radicals,[6] leads us to suggest that other mechanisms, probably involving ionic species, must be operative in the irradiated $CF_4-C_6H_6$ system.

This work is being continued. Details will be reported in subsequent publications.

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[1] The cooperation of Miss Gladys Swope is gratefully acknowledged.

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Infrared Emission Spectra of B₂O₃(g) and B₂O₂(g)†

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THE infrared emission spectrum of the heated vapor of B_2O_3 has been reported by Dows and Porter.[1] They found one band at 2013 cm⁻¹, and observed an isotope shift of about 100 cm⁻¹ when a sample highly enriched in B^{10} was used. They concluded from this that the free B_2O_3 molecule has a bi-pyramidal configuration with D_{3h} symmetry and that extended structures are not admissible.

The reported isotope shift seems unusually large for *any* reasonable molecular model. The suggested bi-pyramidal configuration requires an exceptionally short $B-B$ distance and very unusual bond-angle relationships. The high frequency of the observed emission band strongly suggests that a stretching motion of a boron-oxygen double bond is involved. These and related questions impelled us to continue the investigation of the spectra of the various boron oxides begun independently in this laboratory some time before the above publication appeared.

The B_2O_3 (degassed *in vacuo* for three hours at 800–1000°C) was heated in a molybdenum tube inside an evacuated, water-cooled quartz furnace equipped with NaCl or KBr optical windows. The apparatus will be described elsewhere. The infrared emission was measured in the range 650 to 3500 cm⁻¹ with a Perkin-Elmer Model 99 double-pass monochromator employing a NaCl prism.

Three emission bands at 1350°C were observed with a sample of B_2O_3 having B^{11} and B^{10} isotopes in natural abundance. The band maxima occur at 2041, 1302, and 756 cm⁻¹. When a sample containing 96% B^{10} was examined under identical conditions, the corresponding maxima were found at 2095, 1335, and 762 cm⁻¹. The observed isotope shifts are therefore 54, 33, and 16 cm⁻¹, respectively. The measured shifts are probably somewhat too small, as bands due to the $B^{11}B^{10}$ species (present to about 30%) appreciably overlap and distort the corresponding bands of the $B^{11}B^{11}$ species. When corrected for this, the shifts are 60±3, 37±2, and 17±2 cm⁻¹, respectively. Overlapping resulting from "hot" bands; e.g., 3–2, 2–1, would affect the $B_2{}^{11}O_3$, about equally, and is, therefore, discounted here. The isotope shifts will be further investigated when a sample enriched in B^{11} becomes available.

It is difficult to find any support in the present data for the D_{3h} model. This peculiar structure makes any predictions about its fundamental frequencies hazardous. The observed emission spectrum cannot be used directly either to disprove or confirm the bi-