Reaction of vinyl chloride with *n*-butylamine in tetrahydrofuran, in the presence of $PdCl_2$ and Na_2HPO_4, at room temperature for 168 hr, followed by hydrogenation of the product mixture led to the formation of ethylbutylamine. This is in agreement with similar reactions of ethylene in which isolation of unsaturated products was complicated by formation of stable $PdCl_2$ complexes (*1*).

In all of the above reactions involving vinyl chloride, no reduction of $PdCl_2$ was noted.

A detailed mechanism is not suggested at this time. However, the overall reaction may be viewed as involving formation of a vinyl halide — $PdCl_2$ complex followed either by displacement of the vinylic halogen by a nucleophile from solution or exchange with a nucleophilic ligand. Neither of these processes would result in a net change in the oxidation state of Pd(II). The ease with which these normally difficult reactions occur must be a consequence of the bonding between vinyl halides and $PdCl_2$. A simple view is that the complex structure is similar to that accepted for ethylene-$PdCl_2$ (*5*). Back-donation of electrons from metal to the olefin pi system could then facilitate a displacement by increasing the electron density on the carbon holding the halide.

We are grateful to Professor Harry B. Gray for helpful discussions concerning possible complex structures.

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The Initiation of the Free Radical Thermal Decomposition of Saturated Hydrocarbons by Mercury Perchlorate

Recently Fejes and Emmett (*1*) made use of a mercury perchlorate trap to remove olefins (*2*) from the gas mixture resulting from the cracking of propane, isobutane, and *n*-butane over a silica-alumina cracking catalyst in a circulating system. They concluded that by removing the olefins formed, the surface of the catalyst became covered with methyl carbonium ions. The cracking of these hydrocarbons in the presence of the mercury perchlorate trap resulted in a predominance of methane in the final products and a considerable acceleration in the rate of cracking after a period of 20–30 min.

In an attempt to duplicate these results using a flow reactor we have found that the mercury perchlorate is not inert toward the saturated hydrocarbons. In fact, it reacts with saturated hydrocarbons at room temperature to form volatile species which, upon reaching the reactor furnace (at 470°), are initiators for the homogeneous, thermal decomposition reaction. It has also been found that a mercury perchlorate-hydrocarbon species decomposes explosively if exposed to oxygen.

No acceleration of the cracking rate was observed, nor was the production of methane enhanced by varying the flow rate, the time of reaction, concentration of hydrocarbon, or temperature. The flow rate of *n*-butane (Matheson, instrument grade) was varied by a factor of 10: the time of reaction was varied by allowing *n*-butane to pass over the catalyst at 1000 cc/min for 60 min to 200 min. Whereas, Fejes and Emmett observed an acceleration in rate after 20–30 min, we observed no change. The *n*-butane concentration was varied from 1:10 to 10:1 (butane to nitrogen) by diluting the *n*-butane with nitrogen. The variation of these parameters was examined at 250°, 364°, 470°, 515°C.

Because we found neither an acceleration of the rate of cracking nor an enhancement of methane production by varying the aforementioned parameters, we turned our attention to the mercury perchlorate. In an experiment in which the *n*-butane was diverted through a sample of mercury perchlorate on 60–80 mesh firebrick (*2*) and then allowed to come into contact with the catalyst at 470°C, the conversion increased by a factor of 3 (Fig. 1). Propane is present as an impurity in the *n*-butane in the amount of 0.04% ± 0.01%. As can be seen from Fig. 1, the propane concentration varies only slightly, while the concentrations of methane, ethane, ethylene, and propylene increase drastically when the *n*-butane is allowed to come into contact with the mercury perchlorate. Methane, ethane, ethylene, and propylene are the expected products which would be formed if the decomposition of *n*-butane were occurring by a free radical mechanism (*3*). If we neglect the hydrogen which is formed and calculate the equilibrium concentrations of the four hydrocarbons, we find that the results agree quite nicely with those predicted by the free radical decomposition of *n*-butane. The free radical decomposition predicts methane and propylene each equal to 33.3% and ethane and ethylene each equal to 16.7%. The results shown in Fig. 1 are propylene, 37.6%; methane, 34.5%; ethylene, 14.8%; and ethane, 13.0%. One additional fact should be pointed out. When the *n*-butane was allowed to bypass the mercury perchlorate, the product composition immediately returned to that which had been obtained for the normal cracking of *n*-butane over the silica-alumina catalyst (see last point on Fig. 1).

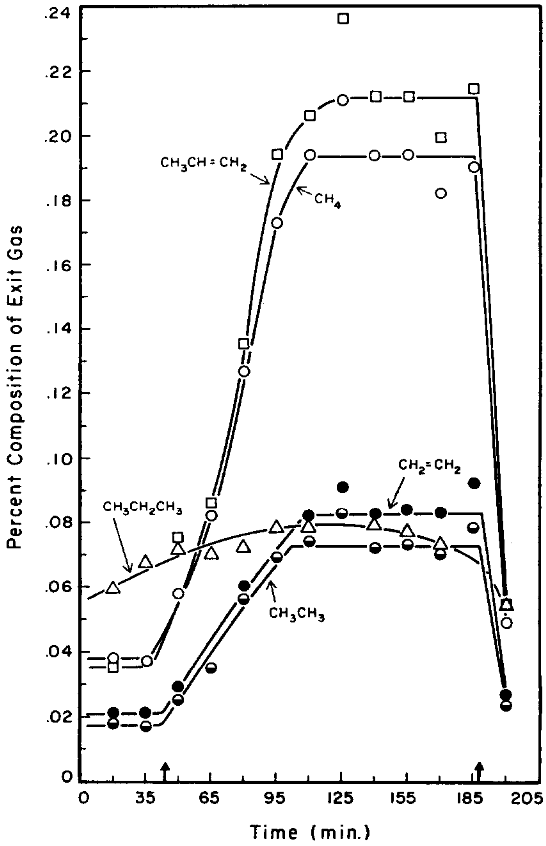

FIG. 1. Effect of mercury perchlorate on the cracking of *n*-butane over Davison silica-alumina. Temperature, 470°; *n*-butane flow, 450 cc/min. The first arrow represents the time at which the *n*-butane was diverted through the mercury perchlorate. The second arrow represents the time at which the *n*-butane was allowed to bypass the mercury perchlorate.

The above experiment provided strong evidence that the decomposition of *n*-butane in the presence of mercury perchlorate was proceeding via a free radical mechanism. In the next series of experiments we decided to investigate the effect of mercury perchlorate in the absence of the silica-alumina catalyst. For this set of experiments the catalyst was removed from the reactor and replaced with an equal volume of 6-mm, hollow glass beads. No decomposition of *n*-butane was noted at room temperature, even in the presence of mercury perchlorate. When the reactor temperature was raised to 470°, a considerable decomposition of *n*-butane was observed, even though the *n*-butane stream was not coming into contact with the mercury perchlorate on firebrick. This initial conversion declined with time, however. We feel that this initial activity of the free radical decomposition is due to the contamination of the reaction system by the earlier experiments with mercury perchlorate. The *n*-butane was allowed to flow through the system for 45 min. During this period the free radical decomposition continued to decline. After the 45-min period the *n*-butane stream was diverted through the mercury perchlorate on firebrick. Almost instantaneously the conversion increased rapidly, and the reaction products were those predicted by the free radical mechanism (Fig. 2). Note also that the concentration of propane which is present as an impurity in the *n*-butane does not change.

Because the mercury perchlorate on firebrick contained a 10% excess of perchloric acid, we became concerned that possibly the excess perchloric acid was being swept off of the firebrick by the butane. The perchloric acid possibly could be the free radical initiator. Two experiments were conducted in order to test this possibility.

First, we pumped on a sample of the mercury perchlorate on firebrick for 19 hr. At the end of this period the pressure was 5×10^{-5} mm Hg. We feel confident that any free perchloric acid would have been pumped off during this period. When *n*-butane was allowed to flow over the pumped sample of mercury perchlorate on firebrick an even greater increase in decomposition occurred as compared to the unpumped mercury perchlorate. Within 15 min after having come into contact with the mercury perchlorate the decomposition increased fivefold (Fig. 3).

We were still not convinced, however, that free perchloric acid did not exist in the mercury perchlorate on firebrick sample. It

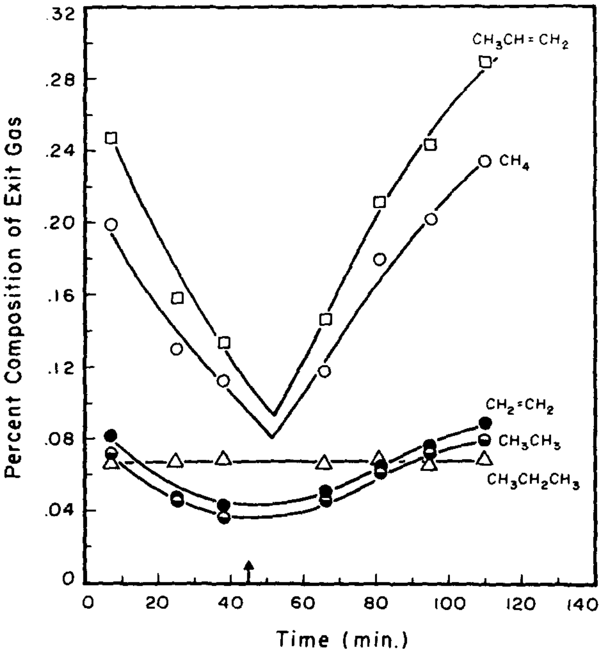

FIG. 2. Effect of mercury perchlorate on the decomposition of *n*-butane over glass beads. Temperature, 470°; *n*-butane flow, 490 cc/min. The arrow represents the time at which the *n*-butane was diverted through the mercury perchlorate.

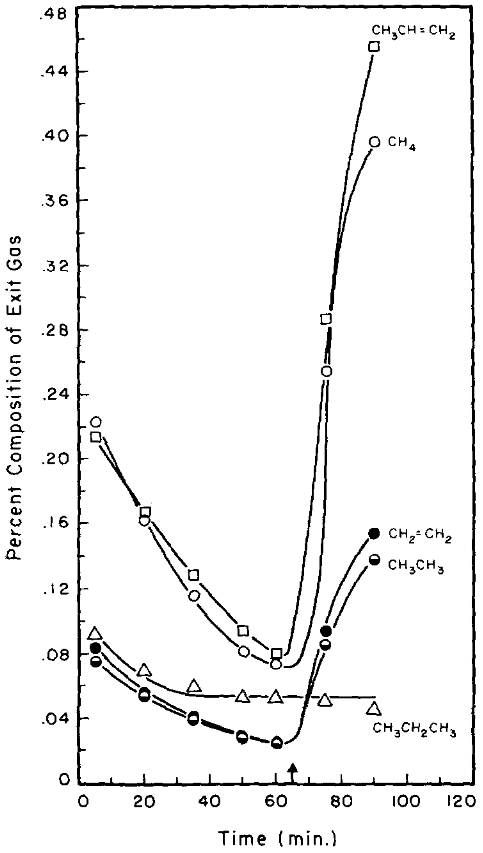

FIG. 3. Effect of "pumped" mercury perchlorate on the decomposition of n-butane over glass beads. Temperature, 470°; n-butane flow, 500 cc/min. The arrow represents the time at which the n-butane was diverted through the mercury perchlorate.

is conceivable that an equilibrium exists between mercury perchlorate and mercuric oxide plus perchloric acid, i.e.,

$$H_2O + Hg(ClO_4)_2 \rightleftarrows HgO + 2HClO_4$$

In order to test such a possibility, we used the pumped sample of mercury perchlorate on firebrick and placed a trap of 8–10 mesh Ascarite between the mercury perchlorate and the glass beads. Hence, any free perchloric acid which might have been swept off of the mercury perchlorate would be trapped by the Ascarite. With this procedure an even more striking result was obtained. Within 5 min after having come into contact with the mercury perchlorate, the decomposition of n-butane again increased fivefold (Fig. 4). But in contrast to the experiment shown in Fig. 3, the product composition appears to have reached equilibrium. Over the next 30 min little change occurs in the product composition. Thus, we have concluded that it is not free perchloric acid which is causing the free radical initiation.

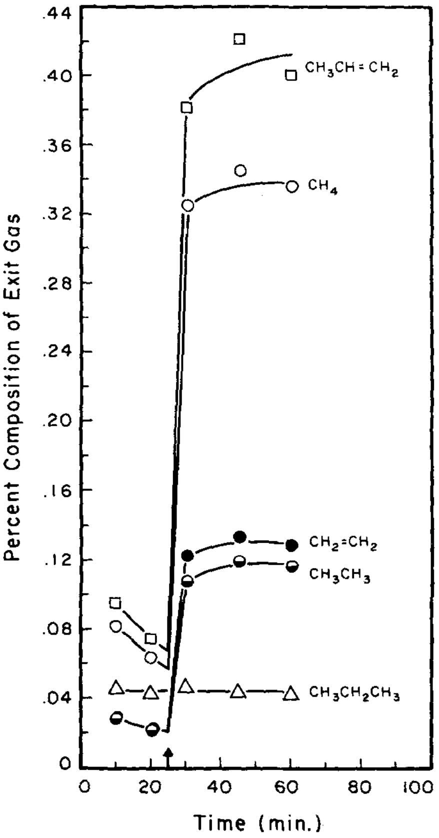

FIG. 4. Effect of "pumped" mercury perchlorate with the addition of an Ascarite trap on the decomposition of n-butane over glass beads. Temperature, 470°; n-butane flow, 500 cc/min. The arrow represents the time at which the n-butane was diverted through the mercury perchlorate and Ascarite.

In an effort to attempt to decide if the initiation was an inherent property of the mercury perchlorate on firebrick, we conducted the following experiment: Nitrogen (500 cc/min) was passed through a pumped sample of mercury perchlorate on firebrick.

An equal flow of *n*-butane was allowed to enter via a separate line. The two gases came together in a mixing bulb and then passed over the glass beads. Under these conditions no enhancement of the butane decomposition was noted over a period of 35 min. As soon as the lines were reversed, i.e., *n*-butane through the mercury perchlorate and nitrogen through the separate line, an immediate fivefold increase in the *n*-butane decomposition was noted. We have thus concluded that the initiator for the free radical decomposition of *n*-butane involves a reaction between the mercury perchlorate and the hydrocarbon. This reaction appears to produce organic perchlorates and possibly, in addition, free radicals such as methyl radical.

The nature of the chain initiator in the reaction vessel is still a matter of speculation. Some evidence as to its nature was revealed by the following experiment involving a violent explosion. The normal procedure for altering reaction conditions was to sweep out the system with nitrogen at 1000 cc/min for 15 min. Oxygen at 100 cc/min was then allowed to flow over the glass beads at 470° overnight in order to burn off any coke deposits. When this procedure was followed after the several successive runs using the highly pumped sample of mercury perchlorate, the mixing bulb exploded violently. We feel that some of the *n*-butane–mercury perchlorate reaction products had concentrated in the mixing bulb. This accumulation is probably what caused a finite free radical decomposition rate (Figs. 2–4) before the *n*-butane had come into contact with the mercury perchlorate. Apparently, after the several successive runs with the pumped sample, the concentration of the *n*-butane–mercury perchlorate reaction products was high enough to cause the violent explosion when they came into contact with oxygen. Because the explosion occurred only in the mixing bulb (it was the only part of the apparatus which shattered), we feel confident that it was not an explosion caused by any residual *n*-butane and oxygen. The amount of *n*-butane remaining in the system after the nitrogen flushing should be very small. We also feel that if it were an explosion between *n*-butane and oxygen, it would have occurred in the reactor, which was at 470°, and not in the mixing bulb, which was at room temperature.

We have also looked at the initiation of the free radical decomposition of propane by the mercury perchlorate on firebrick. The major products, as predicted by the free radical mechanism, were methane and ethylene. This offers additional evidence that the mercury perchlorate in the presence of saturated hydrocarbons forms products which can act as initiators for the free radical decomposition of the hydrocarbon.

It appears that the results of Fejes and Emmett (*1*) can be explained in the following manner. The presence of a sample of mercury perchlorate on firebrick in the circulating gas mixture initiates the free radical decomposition of the hydrocarbons. This free radical decomposition proceeds at a faster rate than the normal cracking reaction. This accounts for the enhancement of rate which they observed. The predominance of methane in the reaction products is just what would be expected from the free radical decomposition of the hydrocarbons when the olefins are removed. The free radical decomposition of propane produces mainly methane and ethylene; of *n*-butane, methane and propylene; and of isobutane, methane, ethylene, and isobutene (*3*). As can be seen, if the mercury perchlorate also traps out the olefins, then the major product in each of the above cases will be methane, as observed by Fejes and Emmett (*1*).

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