intercalation of gadolinium but not europium, nor of yttrium but not dysprosium. Indeed, if ionic size and electron affinity be the sole criteria, then scandium would also intercalate. There appears likewise no correlation between thermodynamic properties of the rare earth chlorides (H_t, S_t, ΔF, etc.) and the extent of their intercalation in graphite.

It is apparent that the rare earth chlorides reside in the graphite lattice ionically without covalent bonding. Croft reports as much from his preliminary magnetochemical studies, and we have confirmed this from magnetic susceptibility measurements on the gadolinium and holmium intercalates. That the rare earth cation accepts electrons from graphite is confirmed by preliminary Hall coefficient studies which we have made. As with intercalated aluminum chloride,[3] positive coefficients have been obtained.

Our X-ray studies have shown little or no measurable variation to occur in dimensions of the graphite lattice upon intercalation; this is in accord with Hennig's observations[11] and reopens the concept of effect of ionic size upon intercalation. If, as Hennig suggests, intercalation occurs only at crystal imperfections, then the ionic size of the cation should be a major factor, not only in the entrapment of the rare earths but also in their removal. This approach can best be exemplified by postulating that rare-earth ions greater than, *e.g.*, gadolinium (1.11 Å.) cannot enter these lattice imperfections, while those ions smaller than, *e.g.*, yttrium (1.06 Å.) cannot be retained on subsequent washing out or treatment with dilute acid. Hennig has calculated that imperfections are approximately 10 μ in length—if the present postulate is correct, a limit of *ca.* 1.11 Å. is therefore set upon the width of the imperfection. This physical entrapment is, we consider, the primary facet of intercalation but still leaves unexplained the differing reactions of yttrium, dysprosium, gadolinium, holmium, terbium and erbium, all between 1.04 and 1.11 Å. ionic radius.

Distinction may be found, however, in considering electronic structures of the consistently intercalated yttrium and gadolinium. Both are tervalent, yttrium has no incomplete inner electron shell, gadolinium has seven 4-f electrons. The gadolinium configuration is generally taken to be of appreciable stability, and the multivalence of samarium, europium and terbium attributable to a tendency for the tervalent ions of these elements to attain the stable 4-f configuration.[12]

Being "internally" stable, the Y^{3+} and Gd^{3+} ions can only be expected to accept electrons into their valence shells, and then only where sufficient ionic interaction exists between them and the anion (Cl^-) such that a resonating structure or hybridization can occur. Where incomplete ionic shells exist, it may be expected that any graphite–chlorine–rare earth resonance or hybridization will so unduly affect the lower lying electrons[13] as to render the whole coördinated structure unstable.

There appear, therefore, the two requirements for intercalation of ionic size (or, most probably, hydrated ionic or associated ion size) and possession of a stable internal electronic structure. These requirements, considered together with those postulated by Mulliken,[6] would appear to establish the model for intercalation of rare earth chlorides in graphite lattices.

Adverting to separational aspects: several rare earth pairs have been examined for preferential intercalation but, from the results obtained, the adequacy of such an approach is found only for yttrium–erbium mixtures (Table II), and this intercalation technique appears suitable for large-scale application. In normal separational systems, even those involving ion-exchange techniques, yttrium adopts a serial position close to dysprosium, holmium and erbium and many precise techniques have been suggested for its removal from these lanthanons—or *vice versa.* Use of this intercalation technique would now appear to render unnecessary anything more than crude separation down to conservative systems before complete extraction of the yttrium can be made; any gadolinium present will accompany the yttrium, but these two elements are so generally separable by, *e.g.*, ferricyanide precipitation that this refinement is of minor importance.

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[12] J. K. Marsh, *Quart. Rev. Chem. Soc. (London)*, **1**, 126 (1947); R. C. Vickery, "Chemistry of the Lanthanons," Butterworth, London, 1953.

[13] R. C. Vickery, *J. Chem. Soc.*, 421 (1952).

[Contribution from the Main Laboratory, South African Coal, Oil and Gas Corp., Ltd.]

Appearance of FeC in a Hydrocarbon Synthesis Catalyst

By J. D. Louw, J. P. van den Berg, L. C. Ferreira and J. J. Pienaar

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The normal equilibrium catalyst in our type of Fischer–Tropsch synthesis reactor contains Hägg iron carbide as a significant component. During the course of a synthesis run a new crystalline phase was discovered in the Debye–Scherrer X-ray diffraction diagram. A deposit from the wall of the reactor was found to consist mainly of this new phase and this material was studied by X-ray diffraction and wet chemical analyses. The X-ray diffraction pattern showed this phase to be identical to the iron carbide previously reported by Eckstrom and Adcock (1950) and designated by them as FeC. Wet chemical analyses support the conclusion drawn from X-ray analyses. Thermomagnetic studies of this material have not yet been possible.

In our hydrocarbon synthesis plant the active catalyst is produced by the action of CO and H_2 at about 20 atmospheres pressure and 315° on promoted and reduced magnetite, analyzing about 95% total iron, in a circulating fluidized bed according to the Kellogg process.

In the course of routine X-ray diffraction analyses on the catalyst in our Synthol plant, it became apparent that at certain stages of certain runs a new crystalline phase was appearing and this eventually reached a more or less stable level after a few days. During the initial stages of the run and after the "conditioning" period of the catalyst, X-ray diffraction diagrams indicate the presence of Fe_3O_4, Hägg carbide and traces of α-Fe only. The appearance of the new phase at a later stage is immediately noticed since it interferes with the evaluation of the relative amounts of Hägg carbide and α-Fe because of an intense interference line at a d/n value of about 2.01 kX. units.

Before the announcement of Eckstrom and Adcock[1] came to our notice, a series of inorganic chemical investigations were carried out in an attempt to identify and evaluate this new crystalline phase in our catalyst. A deposit in the reactor after the completion of a run was found to consist to a very large extent of this unidentified phase with only small amounts of magnetite also present. The material was analyzed carefully by wet chemical methods but, except for the normal small amounts of impurities, no major constituents other than iron and carbon could be detected.

On heating this material containing large amounts of the new phase for 15 minutes at 530° we found by X-rays that large amounts of Fe_3C had formed at the expense of the unidentified phase. In a control experiment, a catalyst sample which yielded a 80:20 ratio of Hägg carbide to magnetite was heated for 30 minutes at 530° and no Fe_3C could then be detected in the X-ray diffraction diagram.

The material, rich in the new phase, was next wax-extracted with xylol, carefully dried and subjected to further analyses. The following information was obtained by X-ray and wet chemical methods of analysis.

X-Ray Diffraction Evaluation.—(a) New unidentified phase—apparently main component; (b) Fe_3O_4—small amount, less than 10%; (c) Hägg carbide—small amount, less than 20%; (d) α-Fe—very small amount, less than 5%; (e) other components—not detected.

Wet Chemical Analyses.—(a) Total iron as Fe, 83.1%; (b) metallic iron as Fe, 80.5%; (c) ferrous iron as Fe, 81.9%; (d) total carbon as C, 14.4%; (e) free carbon as C, 7.0% (nitric acid used).

Analytical Notes.—(a) Total iron was determined by standard volumetric potassium dichromate method. No difficulties were encountered.

(b) Metallic iron was determined on the principle that it converts $FeCl_3$ to $FeCl_2$, the latter then being titrated with standard dichromate. It is obvious, however, that the carbides present reacted as metallic iron, resulting in figures which were too high and altogether unreliable. The existence of a carbide, which reacted as if the Fe and the C are loosely bonded, is therefore indicated.

(c) Ferrous iron was determined by the standard method of dissolving the sample in weak HCl in a protective CO_2 environment and titrating only the reduced form. We found that results obtained in this way are totally unreliable, since the carbides reacted as ferrous iron and some ferric iron might possibly have been reduced to the ferrous state during the dissolution.

(d) Total carbon was determined by the straight-forward combustion absorption method. No difficulties were experienced.

(e) Free carbon determinations were attempted by dissolving the carbides in weak nitric acid, filtering and determining the free carbon in the residue. The high figure found for free carbon could not be reconciled with the normal X-ray diffraction results or with the calculations from other wet chemical figures and it would appear that some of the carbide is liable to decompose to yield undissolved free carbon. This observation would indicate substantial difference in behavior between the carbide of the test sample and the Hägg carbide. The analyses of two standard mixtures of Hägg carbide with magnetite (obtained from the M. W. Kellogg Company) according to the above method yielded the following results

	Standard samples	
	30% Carbide	66% Carbide
Total carbon, %	6.20	13.61
Free carbon, %	3.20	7.05
Combined carbon, %	3.00	6.56
Equivalent Fe_2C	30.9	67.6

Apparently, therefore, free carbon can be determined according to this method in the presence of Fe_2C (considered to be Hägg carbide) only and the behavior of our test material might be due to the presence of a carbide which decomposes in a different manner.

The use of nitric acid might be criticized, since previous investigators made use of a 1:1 HCl solution, which is approximately equivalent in acidity to the 1:2 HNO_3 used in this work. We initially decided upon nitric acid because of its recognized use as a solvent for the spectrophotometric determination of Fe_3C in the laboratories of large steelworks. Nevertheless, when a 1:1 HCl solution was at a later stage used as a solvent with this particular sample, we found that the rate of dissolution was much faster and the reaction more rapid. The free carbon in the residue was found to be even higher, *viz.*, 10.4%, than in the case of the nitric acid treatment. Further evidence of the apparent high reactivity of the iron in the new phase was established by the observation that the relative rate of reduction of $KMnO_4$ solution by the dewaxed new material, was faster than that of a dewaxed catalyst with Fe_2C:Fe_3O_4 ratio of 80:20.

Calculations.—Not being able to determine the metallic Fe or the free carbon, we had to resort to the "oxygen balance" and values obtained by X-ray diffraction to give a probable composition of the material. For the purpose of this paper, the simplified formulas Fe_2C and FeC are assumed, although it is realized that the carbon:iron ratios may be slightly different.

For the material examined:

Fe total, %	83.1
Total C, %	14.4
Impurities, %	1.4
Total	98.9
Oxygen, by balance, %	1.1

This 1.1% oxygen represents 4.0% Fe_3O_4 equivalent to 2.9% Fe. Assume: (a) free iron 4.2% (based on less than 5% X-ray evaluation); (b) Fe_2C 15.0% representing 13.5% Fe equivalent to 1.5% C (based on X-ray evaluation of less than 20%) C.

Subtract the free Fe, Fe derived from Fe_2C and Fe derived from Fe_3O_4 from the total Fe, leaving 62.5% Fe, which, calculated as FeC, represents 75.8% FeC, which is equivalent to 13.3% C.

The probable composition of the sample then is as given below, and according to these figures no free carbon is present, which in our experience is very improbable in this type of catalyst. For some free carbon to be present there must be less FeC than

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[1] H. C. Eckstrom and W. A. Adcock, This Journal, **72**, 1042 (1950).

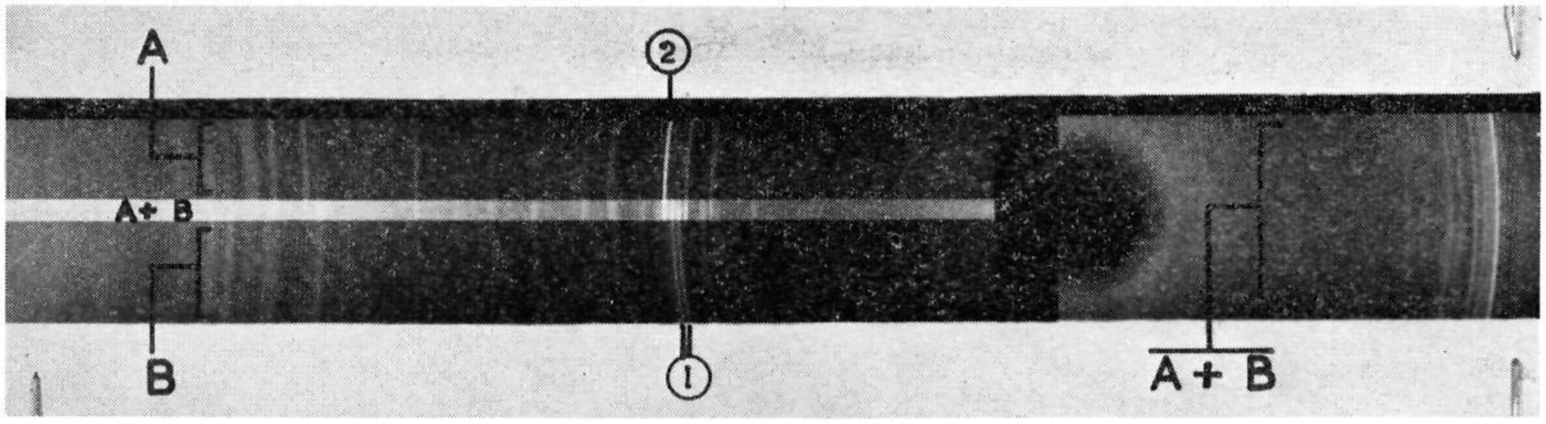

Fig. 1.—A, X-ray interference diagram of almost pure FeC (contaminated by Fe_3O_4); B, X-ray interference diagram of about 90% pure Fe_2C (Hägg); (1) most intense doublet at d = 2.04 and d = 2.07 kX. units; (2) most intense line at d = 2.004 kX. units.

FeC, %	75.8
Fe_2C, %	15.0
Fe, %	4.2
Fe_3O_4, %	4.0
Impurities, %	1.4
Total	100.4
Furthermore:	
Carbon from FeC, %	13.3
Carbon from Fe_2C, %	1.5
Total carbon, %	14.8 against 14.4% actually determined

the calculated 75.8% and more Fe_2C than the assumed 15%.

If, for instance, the Fe_2C is assumed to be 20% representing 18.1% Fe and 1.9% C, we then have 57.9% Fe left, which will form 70.3% FeC binding 12.4% C.

The probable composition then will be

FeC, %	70.3
Fe_2C, %	20.0
Fe, %	4.2
Fe_3O_4, %	4.0
Impurities, %	1.4
Total, %	99.9
Carbon from FeC, %	12.4
Carbon from Fe_2C, %	1.9
Total carbon, %	14.3

This allows for 0.1% free carbon, which is probably still on the low side.

This probable composition fits better with the X-ray diffraction evaluations and, although based on some assumptions, bears out the fact that a carbide like FeC is present.

X-Ray Diffraction Data.—Using Fe Kα radiation, filtered by manganese, the diffraction diagrams obtained with a 114.6 mm. powder camera were studied in more detail. The diffraction lines due to Fe_3O_4, Fe_2C (Hägg) and Fe were eliminated as best we could and the remaining lines were measured and their intensities compared to yield the following data. In the Table I our results are compared with those reported by Eckstrom and Adcock.[1]

TABLE I

X-RAY DIFFRACTION DATA

d/n, kX. units		Relative intensity	
Sasol	Eckstrom and Adcock	Sasol	Eckstrom and Adcock
1.113	1.112	20	10
1.128	1.128	20	10
1.145	1.144	40	25
1.150	1.149	40	25
1.168	1.167	50	30
1.200	1.201	50	35
1.343	1.346	25	15
1.712	1.716	10	15
1.807	1.801	5	30
2.004	2.012	100	100
2.105	2.115	50	45
2.234	2.250	45	35

The conclusion seems to be warranted that the material found to be present in our Synthol catalyst is the same as that reported by Eckstrom and Adcock. We have also found this material to be ferromagnetic, but no facilities for Curie point determinations have as yet been available. However, it can be assumed that the above set of interferences describe a special crystal lattice.

If the observation by Eckstrom and Adcock that this carbide possessed the same Curie temperature as Fe_2C(Hägg) is combined with the facts that the strongest X-ray diffraction line of this carbide almost coincides with both the strongest doublet (d/n = 2.04 and 2.07 kX. units[2–4] of the Hägg carbide and the strongest line (d/n 2.05 kX. units[5]) of α-Fe, it will be appreciated that in the presence of relatively large amounts of both Hägg carbide and α-Fe this carbide will be almost completely unnoticeable by X-ray diffraction or thermomagnetic methods of analysis. This will be even more complicated if a cementite phase, and possibly also H.C.P. carbide, are also present.

The X-ray diffraction pattern of this carbide phase as compared with that of Fe_2C (Hägg) (obtained as 90% pure from the M. W. Kellogg Company) on the same film is shown in Fig. 1.

In Fig. 2 the diffraction patterns of α-Fe and the new carbide are shown on the same film, while Figure 3 gives a similar comparison of a catalyst sample containing Fe_2C, FeC, Fe_3O_4 and α-Fe with an almost pure FeC.

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(2) G. Hägg, *Z. Krist.*, **89**, 94 (1934).

(3) L. J. E. Hofer, *et al.*, THIS JOURNAL, **71**, 189 (1949).

(4) K. H. Jack, *Proc. Roy. Soc.* (*London*), **A195**, 56 (1948).

(5) ASTM X-Ray Diffraction Data Card No. 3347.

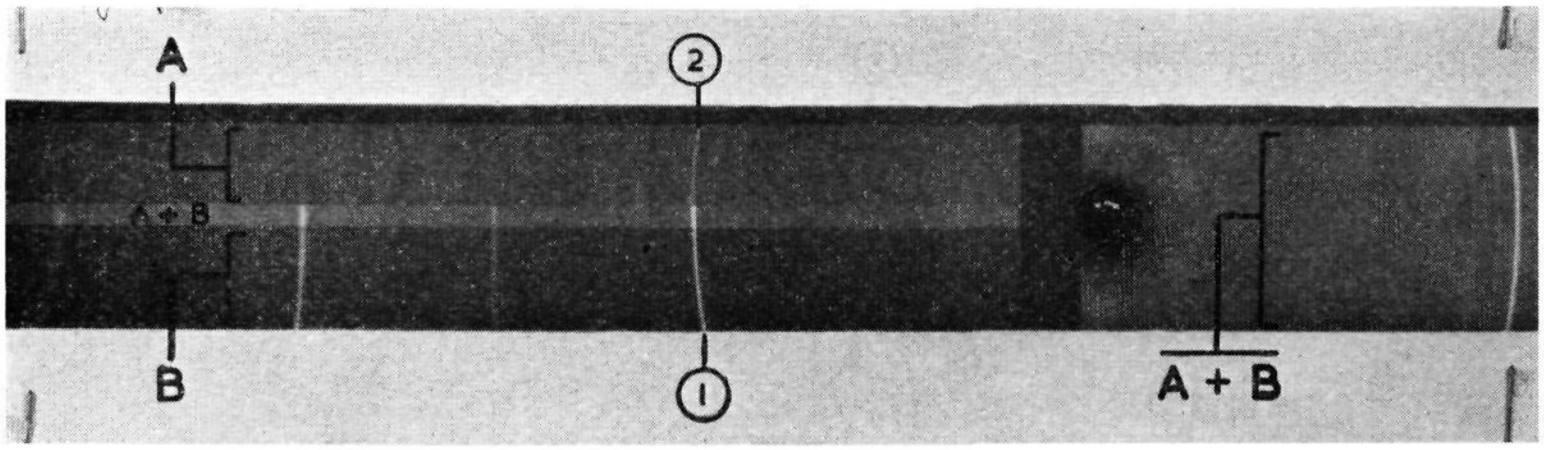

Fig. 2.—A, X-ray interference diagram of almost pure FeC (contaminated by Fe_3O_4); B, X-ray interference diagram of α-Fe; (1) most intense line at $d = 2.05$ kX. units; (2) most intense line at $d = 2.004$ kX. units.

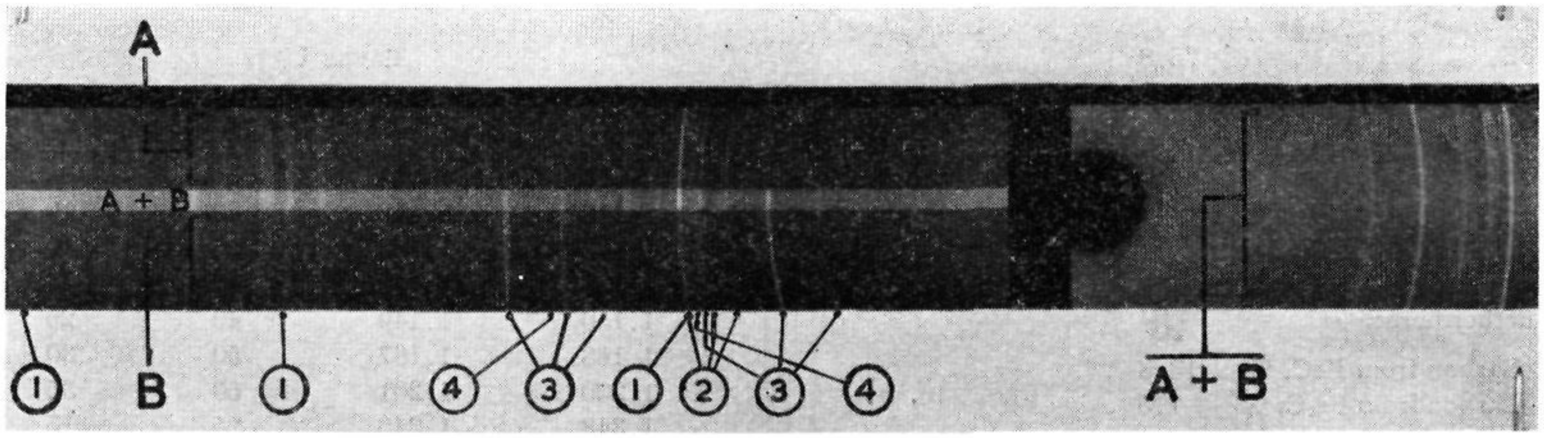

Fig. 3.—A, X-ray interference diagram of almost pure FeC (contaminated by Fe_3O_4); B, X-ray interference diagram of catalyst sample containing Fe_2C, Fe_3O_4, Fe and FeC, where $Fe_2C:Fe_3O_4:Fe$ is approximately 25:25:1 and the relative amount of FeC has not been established: (1) α-Fe; (2) FeC; (3) Fe_3O_4; (4) Fe_2C (Hägg). The cluster of lines due to 1, 2 and 4 which are grouped around the most intense line of FeC ($d = 2.004$ kX. units) is clearly shown.

In all three figures Fe_3O_4 is present as a contaminant in the X-ray diagrams of FeC.

Further work, studying the catalytic behavior, the physical and chemical properties and the mode of formation of this carbide is being continued.

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[CONTRIBUTION FROM THE MICHELSON LAB., U. S. NAVAL ORDNANCE TEST STATION]

Reactions of CD_3 Radicals with the Butenes

BY JAMES R. MCNESBY AND ALVIN S. GORDON

RECEIVED MAY 22, 1957

The photolysis of acetone-d_6 in the presence of each of the four butenes has been carried out. The product analysis is interpreted in terms of two mechanisms, (1) addition of CD_3 to each carbon atom comprising the double bond, and (2) the abstraction by CD_3 of the α-hydrogen atoms of the butene. A striking feature of the methane analyses is that large amounts of CH_4 and CH_3D are produced. This has been interpreted as evidence for addition of CD_3 at a particular position in the double bond in a butene, followed by the loss of a CH_3 radical. Using this interpretation, rate constants for addition of CD_3 to these positions are obtained relative to the rate constant for abstraction of D from acetone-d_6 by the CD_3 radical. For butene-1, addition of CD_3 to the non-terminal carbon atom end of the double bond results in the formation of propylene-d_3. This can be used as a measure of the rate of addition of methyl radicals to the non-terminal carbon atom of the double bond.

The addition of methyl radicals to olefins in the gas phase has been the subject of only a few investigations. Rust and his co-workers[1] examined the products of the reaction of methyl radicals with various olefins in a flow system at 235° and found evidence for non-terminal as well as terminal addition. Raal and Danby[2] indicate that the abstraction of H from acetaldehyde by CH_3 is about three times as fast as addition of CH_3 to the various butenes at 300°.

There is no detailed account in the literature of the mechanism of the reaction of methyl radicals with butene-1.[3] The present work is a report on the reactions of methyl radicals with the four butenes in the temperature range 350–500°.

Experimental

Techniques of photolysis,[4] mass spectrometry,[4] and gas chromatography[5] have been described elsewhere. The 50-cc. cylindrical reaction vessel with plane windows was fabri-

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[1] F. F. Rust, F. H. Seubold and W. E. Vaughan, THIS JOURNAL, **70**, 95 (1948).

[2] F. A. Raal and C. J. Danby, *J. Chem. Soc.*, 2222 (1949).

[3] In the reaction of $CD_3CH_2CH{=}CH_2$ and light methyl radicals, propylene-d_3 has been observed in the products (private communication, Paul Kebarle and W. A. Bryce).

[4] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 4196 (1954).

[5] C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon, *Anal. Chem.*, **28**, 979 (1956).