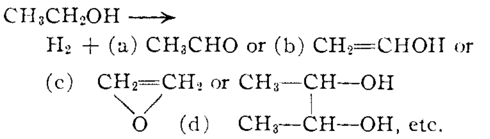
substitution in either the CH_3– or the –OH groups. Thus the formation of radiolytic hydrogen from ethanol must be primarily a radical process (1) since molecular hydrogen formation by a monomolecular process (2) would necessarily be affected by deuterium substitution in at least two of these groups; bimolecular processes (such as (2d)) are excluded by the observed distribution of deuterium in the radiolytic hydrogen (Table I).[4]

$$\text{(a)}\quad CH_3CH_2OH \longrightarrow CH_3CHOH + H \qquad (1)$$

$$\text{(b)}\quad H + C_2H_6O \longrightarrow H_2 + C_2H_5O$$



$$CH_3CH_2OH \longrightarrow H_2 + \text{(a) } CH_3CHO \text{ or (b) } CH_2{=}CHOH \text{ or (c) } \underset{O}{CH_2{=}CH_2} \text{ or (d) } CH_3{-}CH{-}OH,\ CH_3{-}CH{-}OH, \text{ etc.} \qquad (2)$$

In the radical process (1), the hydrogen atoms must originate almost exclusively from $-CH_2-$. A similar conclusion may be deduced from the mass patterns of these deuteroethanols (Table II). In the patterns of both CH_3CH_2OH and in CD_3CH_2OH the peak corresponding to the loss of one hydrogen atom is about twice the size of the parent mass peak. In the pattern for CD_3CH_2OH the peak corresponding to the loss of a deuterium atom is small—*but in the pattern for CH_3CD_2OH the peak corresponding to the loss of one hydrogen atom is very small while the peak corresponding to the loss of a deuterium atom is as large as the parent mass peak.* Thus here also the loss of a hydrogen atom from CH_3CD_2OH occurs largely from the $-CD_2-$ group, despite the opposition offered to this preference by the deuterium isotope effect.[5]

The deuterium content of the radiolytic hydrogen produced from these three alcohols considered in conjunction with the selectivity in hydrogen atom formation (1a) discussed above demonstrates that there must also be a pronounced selectivity in the ensuing abstraction reactions (1b).[4]

It is thus apparent that the production of these radiolysis products from ethanol is not a random process even under conditions where the random process is most favored, *i.e.*, for the formation of hydrogen atoms from carbon–hydrogen bonds which differ only slightly in bond energy, and in the liquid phase where the high collision frequency should prevent equilibration of energy among the various molecular degrees of freedom. It is further apparent that the primary processes leading to loss of hydrogen atoms are similar in the condensed phase and in the gas phase at 10^{-5} mm. pressure. This suggests that the other primary processes observed in the gas phase also occur in the liquid phase but since the corresponding final stable products do not appear[6] these processes must be altered by the influence of the medium, *i.e.*, by a "cage effect" of some sort.

TABLE II

Mass number	46 CH_3CH_2OH	49 CD_3CG_2OH	48 CH_3CD_2OH
50		4.75	
49		100.00	7.18
48		248.80	100.00
47	2.74	46.00	12.50
46	100.00	98.40	100.00
45	205.00	49.25	15.45
44	9.37	28.75	18.40
43	37.80	12.12	17.15
42	12.30	4.94	4.55
41	3.65	2.06	3.68
40	1.60	1.56	1.46
39			2.36
38			3.05

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(4) For the alcohol CH_3CD_2OH, a pure radical process involving only D atoms from the $-CD_2-$ and involving only abstraction from the CH_3- and –OH would produce gas with a maximum H percentage of 50%. Any contribution by the bimolecular process (2d) or by abstraction from the $-CD_2-$ would decrease the percentage of H. The observed percentage of H was 58% (explained by assuming a small contribution of H atoms from the CH_3 and OH). Similar deductions may be made from the data on CH_3CH_2OD radiolyses.

(5) Examination of the mass spectra of CH_3CHDCH_3 (Turkevich, Friedman, Solomon and Wrightson, THIS JOURNAL, **70**, 2638 (1948)), of $CH_3CD_2CH_3$ (Condon, McMurray and Thornton, *J. Chem. Phys.*, **19**, 1010 (1951)), and of $CD_3CH_2CD_3$ (Condon, THIS JOURNAL, **73**, 4675 (1951)) shows that electron impact removes a secondary hydrogen 13–17 times as readily as a primary hydrogen. Similarly electron impact removes a tertiary hydrogen 55 times as readily as a primary hydrogen from 2-methylpropane (Condon, McMurray and Thornton, *loc. cit.*). Finally the mass spectra of $CH_3CDOHCH_3$ (*idem.*, *ibid.*), of $CH_3CHODCH_3$ and $CH_3CDODCH_3$ (Friedman and Turkevich, THIS JOURNAL, **74**, 1666 (1952)) shows that the secondary C–H bond is ruptured more frequently than either the primary C–H bonds or the O–H bond. These data, in conjunction with the data of the present paper, suggest that selectivity in C–H bond rupture is not confined to alcohols (*i.e.*, molecules containing highly electronegative atoms) and that a similar selectivity will be found in gamma irradiation of liquid propane, isobutane, and isopropyl alcohol.

(6) W. McDonnell and A. S. Newton, THIS JOURNAL **76**, 4651 (1954).

(7) Atomics International Division, North American Aviation Co., P.O. Box 309, Canoga Park, Calif.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY JOHN G. BURR, JR.[7]
OAK RIDGE, TENNESSEE

RECEIVED NOVEMBER 16, 1956

INFRARED SPECTRUM OF IRON DODECACARBONYL

Sir:

The infrared spectrum of iron dodecacarbonyl, $Fe_3(CO)_{12}$, has been studied previously by Sheline.[1] He reported two strong absorptions at 2020 and 2043 cm.$^{-1}$ attributable to C–O stretching of ordinary (end-group$^{(2)}$) carbon monoxide groups; a third band at 1833 cm.$^{-1}$ was considered to be associated with the presence of ketone-like bridging carbon monoxide group(s) in the molecule. The validity of three possible models for the molecule was considered in the light of these data and it was concluded from symmetry arguments that the most likely structure was a linear one, which, in the nomenclature used previously,[2] would be 4–2–2–4, the two groups of two carbon monoxides forming ketonic bridges.

We have reinvestigated the infrared spectrum of $Fe_3(CO)_{12}$ in the C–O stretching region using both rock salt and lithium fluoride optics and also in the cesium bromide region; our observations are sum-

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(1) R. K. Sheline, THIS JOURNAL, **73**, 1615 (1951).

(2) F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).

marized in the table. For the following reasons, we believe that the structure proposed by Sheline is untenable.

Principal Infrared Absorption Bands of $Fe_3(CO)_{12}$[a]

Frequency, cm.$^{-1}$	Relative[b] intensity
2043	10
2020	8
1997	~4
1858	~0.5
1826	~0.5
594	...
575	...

[a] Solvents: CS_2, CCl_4, $CHCl_3$. [b] Estimated from a plot of (cm.$^{-1}$ × optical density) *vs.* cm.$^{-1}$ for the spectrum in CS_2 in which the best resolution was obtained.

The extremely low relative intensity of the absorption in the region 1820–1860 cm.$^{-1}$ strongly suggests that the bands are not fundamentals, and hence that there are no ketonic bridging carbon monoxide groups of the type previously proposed for $Fe_2(CO)_9$,[3] and $CO_2(CO)_8$.[4] Furthermore, if the spectra are taken in CS_2, CCl_4 or $CHCl_3$, rather than the toluene used previously,[1] two bands are clearly discernible; the model favored by Sheline would produce only one fundamental in this region.

Although only two bands at ~2000 cm.$^{-1}$ are observed using rock salt optics (*cf.* also ref. 1), a third band at ~1997 cm.$^{-1}$ is resolved easily with a lithium fluoride prism. Throughout the range 450–3000 cm.$^{-1}$ the only other significant absorptions were the two bands at 594 and 575 cm.$^{-1}$, which seem best assigned as carbon–metal stretching frequencies. It is possible to assign the very weak bands at 1858 and 1826 cm.$^{-1}$ as triple combinations among the metal–carbon stretching frequencies, an assignment more in keeping with their low intensity.

Before any conclusion can be reached concerning the structure of the free molecule, $Fe_3(CO)_{12}$, the band at 1997 cm.$^{-1}$ must be assigned. There are three main possibilities: (i) that it is a fundamental, though it is perhaps a little weak; (ii) that it is a combination involving one of the other C–O stretching frequencies, but this would require the presence of a fundamental frequency at least as low as ~50 cm.$^{-1}$, which would seem unlikely although not impossible; (iii) that it is the C^{13} analog of the 2043 cm.$^{-1}$ band which would be expected in this position, but our estimate of the relative intensities (~$^1/_{100}$ expected) seems to rule this out. If the 1997 cm.$^{-1}$ band is in fact a third fundamental, then another structure (IV) considered by Sheline involving an equilateral triangle of three iron atoms bonded directly to one another is again eliminated.

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(3) R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

(4) J. W. Cable, R. S. Nyholm and R. K. Sheline, *ibid.*, **76**, 3375 (1954).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS. F. A. COTTON
DEPARTMENT OF CHEMISTRY
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
LONDON, ENGLAND G. WILKINSON

RECEIVED OCTOBER 15, 1956

A NOVEL REARRANGEMENT OF N-BROMOSUCCINIMIDE

Sir:

We have found that the reaction of N-bromosuccinimide (NBS) with allyl chloride, allyl bromide, or β-methallyl chloride in chloroform solution with trace quantities of benzoyl peroxide yields β-bromopropionyl isocyanate $BrCH_2CH_2CONCO$ (I). The product was isolated by distillation at reduced pressure to yield I, b.p. 68–69° (10 mm.), n^{27}D 1.4915, intense infrared absorption maxima, *inter alia*, at 2250, 1735, and 1400 cm.$^{-1}$. A mass spectrometer was used to obtain the molecular weight (calcd.: 177; found, 177); the cracking pattern was consistent with the postulated structure.

Reaction of I with water gave carbon dioxide and β-bromopropionamide,[1] m.p. 115–116° (from chloroform), undepressed by admixture with a sample prepared from β-bromopropionyl bromide and ammonia. Reaction of I with methanol gave colorless needles (II), m.p. 137–138° (from methanol). *Anal.* Calcd. for $C_5H_8O_3NBr$: C, 28.60; H, 3.84; N, 6.67; Br, 38.05. Found: C, 28.7; H, 3.8; N, 6.5; Br, 38.0. Reaction of I with aniline in methylene chloride yielded colorless needles (III), m.p. 181–183° (from methanol). *Anal.* Calcd. for $C_{10}H_{11}N_2O_2Br$: C, 44.30; H, 4.09; N, 10.33; Br, 29.47. Found; C, 44.7; H, 4.3; N, 10.3; Br, 29.3. The infrared spectra of II and III were consistent with their formulation as methyl β-bromopropionylcarbamate and N-phenyl-N′-β-bromopropionyl urea, respectively.

To synthesize I, β-bromopropionic acid was treated with phosphorus tribromide in benzene to yield 59% of β-bromopropionyl bromide, b.p. 50–52° (4 mm.), n^{27}D 1.5320. *Anal.* Calcd. for $C_3H_4OBr_2$; C, 16.67; H, 1.87; Br, 74.03. Found: C, 16.4; H, 1.7; Br, 74.4. Treatment of the acid bromide with dry, powdered silver cyanate[2] gave 40% I, b.p. 68–69° (10 mm.), n^{29}D 1.4900, infrared spectrum superimposable on that of I isolated from the NBS reaction. *Anal.* Calcd. for $C_4H_4NO_2Br$; C, 26.99; H, 2.26; N, 7.87; Br, 44.90. Found: C, 26.9; H, 2.3; N, 7.8; Br, 44.9. Samples of II and III prepared from this sample of I had m.ps. of 137–138° and 183–184°, respectively, undepressed by admixture with the previously described samples. The infrared spectra of the samples of II and III from both sources were identical.

No satisfactory analysis of I isolated from the reaction of NBS has been obtained as yet; a typical analysis is shown. *Anal.* Calcd. for $C_4H_4NO_2Br$: C, 26.99; H, 2.26; N, 7.87; Br, 44.90. Found: C, 26.8; H, 2.5; N, 7.2; Br, 49.0. Mass spectra indicated the presence of 1–2% of a chlorobromopropene in the sample; X-ray absorption indicated the same sample contained 45 ± 1% Br and 2 ± 1% Cl. Presumably the chlorobromopropene was responsible for the discrepancy in the analytical data.

The identity of the samples of I from the reaction of NBS with allyl chloride, allyl bromide, and

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(1) C. S. Hamilton and C. L. Simpson, THIS JOURNAL, **71**, 3158 (1924).

(2) O. C. Belliter, *Ber.*, **36**, 3213 (1903).