On the Crystal Structure of Carotenoids

BY G. MACKINNEY

In Table I are listed x-ray powder patterns of various carotenoid preparations. Though describing no patterns, Karrer and co-workers[1] state that no differences were detectable between carotene, xanthophyll, and lutein. Such results may be caused by oxidation, as powdered xanthophylls in particular are unstable, and should be exposed *in vacuo.* Patterns were obtained by exposure *in vacuo* of powdered crystalline material to the Kα radiation of molybdenum.

TABLE I

INTERPLANAR SPACINGS IN ÅNGSTRÖM UNITS

I, Carotene

a, Carrot roots 1. $CHCl_3$–pet. ether	2. CS_2–EtOH	b, Spinach[a] cauliflower[a] sunflower leaves 1. $CHCl_3$–EtOH
7.53 w	7.50 w	7.51 w
6.04 s	5.96 s	6.10 s
5.70 s	5.68 s	5.73 s
5.28 w	5.31 w	5.27 w
..	5.00 w	5.02 w
4.69 w	4.67 w	4.70 w
..	4.40 w	4.41 w
4.07 s	4.04 s	4.08 s
3.77 w	3.81 w	3.79 w
3.60 s	3.60 s	3.59 s
..	..	3.33 vw
3.02 vw	..	3.01 vw

II, Leaf Xanthophyll		III, Lutein	IV, Lycopene[a]
a, MeOH[a]	b, $CHCl_3$–pet. ether	CH_2Cl_2–*n* heptane	CS_2–EtOH
6.60 m	6.55 s	6.70 m	
..	..	6.00 w	5.79 s
5.51 m	5.40 m	5.50 m	5.27 s
5.10 w	4.95 w	5.00 w	4.90 s
4.61 w	4.5–4.2 band	4.40–4.15 band	..
3.91 s	4.05 s	4.08 s	4.14 w
3.70 m	..	3.80 m	3.97 s
3.53 s	3.65 s	3.66 s	3.62 s
		3.30 w	3.43 s
			3.18 vw
			3.00 vw

[a] Samples provided by courtesy of Dr. James H. C. Smith. s = strong, w = weak, etc.

The carotenes, from carrot roots and the leaves of spinach, cauliflower and sunflower, were variously recrystallized with EtOH and petroleum ether from CS_2 and $CHCl_3$. Xanthophyll, from sunflower leaves, was recrystallized from MeOH, and from $CHCl_3$–petroleum ether. Lutein was isolated from its ester, helenien, in sunflower petals and precipitated from CH_2Cl_2–*n*-heptane. Lycopene, from tomatoes, was recrystallized from CS_2–EtOH.

No spacings longer than 7.53 Å. were observed, though the range explored would have recorded up to 15 Å. One may estimate that no first order reflections have been photographed. Spacings longer than 6.0 Å. were measured within ±0.05 Å., and the error falls rapidly with increase in the angle of reflection.

The similarity of the carotene preparations is noteworthy. With no significant variation in pattern, it seems improbable that carotene takes up ethanol of crystallization. Between lutein and leaf xanthophyll, there is no significant difference. In the samples used, $[\alpha]^{20}_{6678}$ for lutein was $+128°$ (25.8 mg. in 15 cc. of $CHCl_3$) and for xanthophyll, $+107°$ (7.0 mg. in 15 cc. of $CHCl_3$). The latter is probably a mixture containing chiefly lutein.

Certain similar interplanar spacings suggest many common structural features in these large carotenoid molecules, but definite differences, both of spacing and intensity, are to be noted in the x-ray diffraction powder patterns of carotene, leaf xanthophyll and lutein, and lycopene.

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(1) Karrer, *et al.*, *Helv. Chim. Acta*, **14**, 614 (1931).

Elementary Organic Reactions

BY F. O. RICE

In connection with the work in this Laboratory on the decomposition of organic compounds through a free radical mechanism,[1] it has been necessary to assume definite values for the activation energies of a number of simple organic reactions. It seems desirable to list these reactions together with the activation energies assigned and discuss briefly the somewhat conflicting evidence available.

(1)	$H + CH_4 \longrightarrow H_2 + CH_3$	> 20
(3)	$H + C_2H_6 \longrightarrow H_2 + CH_3CH_2$	17
(5)	$CH_3 + H_2 \longrightarrow CH_4 + H$	23
(7)	$CH_3CH_2 + H_2 \longrightarrow C_2H_6 + H$	25
(9)	$CH_3 + C_2H_6 \longrightarrow CH_4 + CH_3CH_2$	20
(11)	$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2$	15
(13)	$CH_3 + CH_3OCH_3 \longrightarrow CH_4 + CH_3OCH_2$	15
(15)	$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO$	15
(2)	$CH_4 \longrightarrow CH_3 + H$	100

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(1) Rice, THIS JOURNAL, **53**, 1950 (1931); Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

(4)	$CH_4 \longrightarrow CH_2 + H_2$	100
(6)	$CH_3 \longrightarrow CH_2 + H$	100
(8)	$C_2H_6 \longrightarrow 2CH_3$	79.5
(10)	$CH_3CH_2 \longrightarrow C_2H_4 + H$	49
(12)	$CH_3COCH_2 \longrightarrow CH_2{=}CO + CH_3$	48
(14)	$CH_3OCH_2 \longrightarrow HCHO + CH_3$	38
(16)	$CH_3CO \longrightarrow CO + CH_3$	10

Reactions (2) and (4).—The temperature coefficient of the decomposition of methane into free radicals has been measured[2] according to a technique previously described.[3] It was not possible to determine from the data obtained whether Reaction (2) or Reaction (4) was the primary reaction;[4] accordingly we have assigned the measured value for the dissociation of methane into free radicals to each of these two reactions; this measured value must then be regarded as the minimum possible in each case.

Reaction 6.—Following the suggestion of Mecke[5] that the second hydrogen atom of methane may be much more loosely bound than the first hydrogen, it would seem probable that methyl groups should be somewhat unstable and therefore Reaction (6) should require a relatively small energy of activation. This is, however, not in accord with our experimental work on the decomposition of organic compounds into free radicals. The decomposition of such compounds as acetone,[6] propane,[6] ethane[7] and methane[2] yields chiefly methyl groups which must therefore be at least as stable as the compounds from which they are formed; consequently we have assigned 100 Cal. as the minimum value for the activation energy of Reaction (6).

Reaction 8.—The activation energy of the reaction $C_2H_6 \longrightarrow 2CH_3$ has recently been measured experimentally[7] and the value obtained seems reasonable in view of recent estimates of 75–80 Cal. for the strength of the C–C bond.[8]

Reaction 10.—Ethyl groups have been prepared by the decomposition[9] of lead tetraethyl in a current of nitrogen and recently the activation energy of the decomposition of lead tetraethyl has been measured[10] and found to be 37 Cal. This gives a minimum value for Reaction (10); the value assigned agrees best with the free radical mechanism.[1]

Reactions (12), (14) and (16).—The values for these reactions have been assigned chiefly on the basis of a free radical mechanism.[1] The acetyl radical CH_3CO (Reaction (16)) is probably very unstable; we have found that diacetyl[11] is absent in the products obtained when acetone is decomposed into free radicals at low pressures;[6] furthermore, the presence of diacetyl does not seem to have been reported among the products of the photochemical decomposition of ketones or aldehydes although it seems likely that in at least some cases the acetyl radical may have been formed.

Reactions (1) and (3).—The value adopted for Reaction (3) is that best suited to the free radical mechanism;[1] however, experiments on the direct combination of atomic hydrogen and ethane[12] suggest a somewhat lower value; it does not seem possible to make more than a very approximate estimate[13] because of our lack of knowledge of the temperature. Reaction (1) must have a much higher activation energy than Reaction (2) since methane does not react with atomic hydrogen under conditions under which ethane reacts readily.

Reactions (5) and (7).—The value of 8 Cal. obtained by von Hartel and Polanyi[14] for Reaction (5) ($CH_3 + H_2 \longrightarrow CH_4 + H$) leads to the result that at 600°C. only $e^{8000/2 \times 873} \sim 100$ collisions of CH_3 and H_2 would be required for reaction; if this low value were correct, it is doubtful whether it would even be possible to prepare methyl radicals by decomposing lead tetramethyl in a current of hydrogen. Actually we have performed this experiment under conditions such that several thousand collisions between CH_3 and H_2 occurred at 600° and we believe that 20 Cal. is a minimum value for this reaction. Recently Leermakers[15] has shown that the activation energy of the corresponding Reaction (7) for ethyl groups must be greater than 15 Cal. The values assigned to these two reactions are those which fit best the free radical mechanism.

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(2) Rice and Dooley, unpublished work.

(3) Rice and Johnston, This Journal, **56**, 214 (1934).

(4) We found that the fragments were mainly methyl groups, but these might be produced by reaction (4) followed by the reaction $CH_2 + CH_4 \longrightarrow 2CH_3$. If the reaction $CH_2 + CH_4 \longrightarrow C_2H_6$ occurred [see Kassel, *ibid.*, **54**, 3949 (1932)] there would be no mirror removal under our conditions.

(5) Mecke, *Z. physik. Chem.*, **B7**, 108 (1930); *Z. Elektrochem.*, **36**, 595 (1930).

(6) Rice, Johnston and Evering, This Journal, **54**, 3529 (1932).

(7) Rice and Dooley, *ibid.*, **55**, 4245 (1933).

(8) Conant, *J. Chem. Physics*, **1**, 427 (1933); Kistiakowsky and Gershinowitz, *ibid.*, **1**, 432 (1933).

(9) Paneth and Lautsch, *Ber.*, **64**, 2708 (1931).

(10) Leermakers, This Journal, **55**, 4508 (1933).

(11) Unpublished work with B. L. Evering.

(12) See Chadwell and Titani, This Journal, **55**, 1363 (1933), for a review of the literature.

(13) Dr. L. Kassel (private communication) estimates 12.5 Cal. for the $H + C_2H_6$ reaction based on an assumed temperature of 450°K. in Chadwell and Titani's experiments.

(14) Von Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).

(15) Leermakers, This Journal, **55**, 4508 (1933).

Reactions (9), (11), (13) and (15).—There does not seem to be any experimental evidence available for these reactions and in these cases also we have assigned values which are in agreement with the free radical mechanism.

DEPARTMENT OF CHEMISTRY
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Ammonolysis of Fluorenone and Fluorenone Anil

BY LOUIS A. PINCK AND GUIDO E. HILBERT

Strain[1] has shown that ketones, such as acetophenone, on heating with ammonia at 180° with aluminum chloride as a dehydrating agent, yield the corresponding ketimines. It has now been found that fluorenone imide can be prepared in excellent yield by the interaction of fluorenone and ammonia at room temperature. This method is superior to that of Kliegl[2] and is recommended for preparative purposes. Benzophenone, 9,9-dichlorofluorene and 1,2-dichlorodibiphenylene-ethane under similar conditions, however, do not react.

Additional information on the behavior of Schiff bases in liquid ammonia[3] was obtained in a study of the ammonolysis of fluorenone anil. This reaction leading to the formation of fluorenone imide and aniline was catalyzed by ammonium chloride and did not go to completion; apparently an equilibrium was attained. Fluorenone anil was readily prepared by heating fluorenone imide and aniline.

Experimental Procedure

Ammonolyis of Fluorenone.—Ten grams of fluorenone[4] was treated with 15 cc. of sodium-dried ammonia and allowed to stand at room temperature for several weeks. After the removal of ammonia the fluorenone imide was recrystallized from ligroin; m. p. 124°, yield practically quantitative.

Fluorenone Anil.—A mixture of 0.2 g. of fluorenone imide and 0.2 cc. of aniline was heated at 120° for ninety minutes; ammonia was evolved. The yellow sirupy reaction product solidified on cooling and was recrystallized from petroleum ether; m. p. 87°.[5]

Ammonolysis of Fluorenone Anil.—A solution of 0.5 g. of fluorenone anil and 0.25 g. of ammonium chloride in dry liquid ammonia was heated at 60° for four days. The ammonia was removed and the reaction product dissolved in boiling ligroin. On concentration of the solution 0.22 g. of fluorenone imide separated. From the mother liquor was isolated 0.15 g. of unchanged anil.

No fluorenone imide was isolated in an experiment in which a solution of fluorenone anil in dry ammonia was heated at 60° for twenty hours.

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(1) Strain, THIS JOURNAL, **52**, 820 (1930).

(2) Kliegl, *Ber.*, **43**, 2488 (1910); see also Goldschmidt and Beuschel, *Ann.*, **447**, 203 (1926).

(3) Strain, THIS JOURNAL, **50**, 2218 (1928).

(4) This was prepared according to the method of Schmidt and Wagner, *Ber.*, **43**, 1796 (1910), (3 kilos of technical fluorene yielded 2450 g. of pure fluorenone), which is practically identical with that recently published by Huntress, Hershberg and Cliff, THIS JOURNAL, **53**, 2720 (1931).

(5) Reddelien, *Ber.*, **43**, 2479 (1910); Schlenk and Bergmann,, *Ann.*, **463**, 292 (1928).

CONTRIBUTION FROM THE
BUREAU OF CHEMISTRY AND SOILS
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COMMUNICATIONS TO THE EDITOR

TWO TYPES OF ACTIVATED ADSORPTION OF HYDROGEN ON THE SURFACE OF A PROMOTED IRON SYNTHETIC AMMONIA CATALYST

Sir:

By making adsorption measurements in conjunction with our study of the catalytic conversion of ortho to para hydrogen we have obtained data that seem to establish definitely the existence of two types [see Benton, *Trans. Faraday Soc.*, **28**, 202 (1932), and Langmuir, *Chem. Rev.*, **13**, 188 (1933)] of activated and one type of physical adsorption of hydrogen on the surface of an iron catalyst promoted with 1.3% Al_2O_3 and 1.59% K_2O. The characteristics of the three types of adsorption on the promoted iron catalyst are as follows.

Physical Adsorption. The adsorption of hydrogen at 760 mm. pressure by a 10-cc. (about 22-g.) sample of catalyst that had been reduced by hydrogen at 450° and degassed at the same temperature, was 5.0, 2.8 and 0.25 cc. at -196, -183 and $-144°$, respectively. The heat of adsorption calculated from isotherms was about 2000 calories.

Type A Activated Adsorption.—Between -78 and 0° apparent equilibrium could be obtained in