tions of 100 cc. of chloroform. The chloroform extracts were combined, washed with dilute ice cold 3% sodium bicarbonate and then with ice water, the chloroform layer separated and dried over calcium chloride. Upon evaporation at gentle heat aided by an air current, a finely divided crystalline deposit was obtained. Filtered and washed with ether the yield was 18.0 g. (54%). The mother liquors yielded further material on concentration, the average yield being about 70%.

The compound could be recrystallized readily and practically quantitatively from 15 parts of boiling 95% alcohol; 6.3 g. recrystallized from 90 cc. of 95% alcohol gave a yield of 5.8 g. of material whose $[\alpha]^{20}_{D}$ value was −88.3° (0.2109 g. in 25 cc. $CHCl_3$ rotated 1.49° to the left). A further single recrystallization gave −88.4° (0.1485 g. in 25 cc. $CHCl_3$ rotated 1.05° to the left). It can also be recrystallized without decomposition from water at 80–90°, being soluble to the extent of about 0.4 g. in 100 cc.

The compound crystallizes in colorless brilliant needles 2 to 3 mm. long and melts at 201° (corr.) to a clear colorless oil.

An analysis for acetyl groups by the method of Kunz and Hudson showed the presence of four acetyl groups, 0.2378 g. substance consumed 20.30 cc. of 0.1 *N* sodium hydroxide; calcd. 20.14 cc.

Anal. Calcd. for $C_{20}H_{23}O_{13}$: C, 50.94; H, 4.92. Found: C, 50.83; H, 5.29.

5-β-*d*-Glucosidokojic Acid (2-Hydroxymethyl-5-β-*d*-glucosido-1,4-pyrone).—Attempts to deacetylate the tetraacetyl compound by ammonia in methyl alcohol solution were not successful. Incomplete deacetylation resulted even after allowing the deacetylation mixture to remain overnight, followed by gentle refluxing and resaturation of the resultant solution with ammonia and subsequent standing. However, sodium methylate brought about the desired result very smoothly.

Nine grams of the tetraacetylglucosidokojic acid was dissolved by warming in 300 cc. of chloroform and cooled to 10°. A solution of 75 cc. of 0.9 *N* sodium methylate and 25 cc. of anhydrous methyl alcohol was added and the mixed solutions allowed to stand in the ice-bath for one-half hour. A white gelatinous precipitate came down. The suspension was treated with the exact amount of dilute sulfuric acid to neutralize the original amount of sodium methylate and concentrated *in vacuo* at 60° to dryness. The dry residue was extracted with 75 cc. of 95% alcohol and the extract concentrated *in vacuo*. Colorless needles separated as the solution concentrated and the resulting yield of crude material was 2.8 g. The substance was recrystallized from 5 parts of 95% alcohol. The recrystallized glucoside gave $[\alpha]^{20}_{D}$ −107.2° in water (0.1797 g. in 25 cc. H_2O rotated 1.54° to the left) and a further recrystallization gave −107.4° (0.1470 g. in 25 cc. H_2O rotated 1.26° to the left); therefore the value −107.3° is accepted as the true rotation. The compound melts at 197–198° (corr.) to a clear colorless oil.

Anal. Calcd. for $C_{12}H_{16}O_9$: C, 47.35; H, 5.30. Found: C, 47.42; H, 5.66.

The writer wishes to express appreciation for the assistance of Dr. F. H. Goldman in the analyses.

Summary

Kojic acid (2-hydroxymethyl-5-hydroxy-1,4-pyrone) has been condensed with acetobromoglucose to form 5-β-tetraacetyl-*d*-glucosidokojic acid. By deacetylation of this acetate with sodium methylate crystalline 5-β-*d*-glucosidokojic acid has been isolated and characterized.

WASHINGTON, D. C. RECEIVED DECEMBER 1, 1933

NOTES

Auto-Oxidation and Ionization Potentials of Molecules

BY NICHOLAS A. MILAS

Some years ago[1] the writer showed that the tendency to auto-oxidize of the hydrides, alkyl and aryl derivatives of the elements of the fifth group of the periodic table increases as the "effective nuclear charge" of these elements increases. This seems to be true also with similar derivatives of the elements of the sixth and seventh groups. Diethyl telluride, for example, is far more easily oxidized than diethyl ether. Similarly, ethyl iodide is more easily oxidized than ethyl chloride. If the auto-oxidation of these substances proceeds through a preliminary addition of molecular oxygen to the reactive unshared electrons present in each molecule, then there ought to exist a relationship between the tendency of these substances to auto-oxidize and the ionization potentials of the reactive electrons.

If one makes a simple calculation of the ionization potentials of the hydrides of these elements, on the assumption that the ratio of the first ionization potentials of any two elements in each group varies directly as the ionization potentials of their hydrides, one would find that the ionization potentials of the different hydrides are inversely proportional to their tendency toward auto-oxidation. The ionization potential of NH_3, for example, is 11.2 volts[2] while that of

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(1) Milas, *J. Phys. Chem.*, **33**, 1204 (1929).

(2) Mackay, *Phys. Rev.*, **24**, 319 (1924); "Handbuch der Physik," **23**, Part 1, 142 (1933).

BiH_3 is about 5.6 volts (calcd.). Similarly, the ionization potential of H_2O is 13.2 volts,[2] while that of H_2Te is 8.7 volts (calcd.). A similar trend is found with the hydrides of the seventh group. In other words, as one passes down in each group of the hydrides, from the lightest to the heaviest central element, there is a regular decrease in the ionization potentials, which means an increase of looseness of the reactive unshared electrons. With an increase of looseness of these electrons there is a relative increase in the tendency toward auto-oxidation.

RESEARCH LABORATORY OF
ORGANIC CHEMISTRY
CONTRIBUTION NO. 102
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.

RECEIVED OCTOBER 17, 1933

The Reduction of Aliphatic Cyanides and Oximes with Sodium and *n*-Butyl Alcohol

BY C. M. SUTER AND EUGENE W. MOFFETT[1]

The usefulness of *n*-butyl alcohol in the sodium reduction of a number of aliphatic cyanides and oximes has been investigated. In a considerable number of preliminary experiments upon the reduction of *n*-butyl cyanide it was found that: (1) better results were obtained by adding the sodium to the boiling solution of the cyanide than by adding the cyanide solution to the sodium; (2) if the temperature of the reaction mixture were kept below the boiling point mechanical stirring increased the yield of amine, but it was of no advantage to stir the refluxing solution; (3) the use of more than 7 atoms of sodium per mole of cyanide did not appreciably increase the yield of amine; and (4) all of the sodium dissolves within a convenient time if slightly more than 3 moles of *n*-butyl alcohol is used per atom of sodium. It is probable that (3) would not be true for all reductions of this type.

The yields of amines from a series of methyl alkyl ketoximes varied from 69 to 86% of the theoretical amounts. Heptaldoxime gave 69% of the amine. *n*-Butyl and *n*-amyl cyanide gave 86 and 78%, respectively, of the corresponding amines.

Procedure.—A solution of 1 mole of cyanide or oxime in 2300 cc. of *n*-butyl alcohol in a 5-liter two-necked flask fitted with a 2.5 × 100 cm. Pyrex condenser was heated to boiling and 161 g. (7 moles) of sodium added in 10–20 g. pieces at short intervals through the large neck of the flask. This required from ten to fifteen minutes. After the reaction had moderated the mixture was refluxed until practically all of the sodium had dissolved. The reaction mixture was allowed to cool, 1.5 liters of water added and the mixture distilled to remove the amine and alcohol. More water was added as necessary. The distillate was made slightly acid with hydrochloric acid and distilled to a volume of 300 cc., 500 cc. of water added and distillation continued until no more alcohol came over. The water solution of amine hydrochloride was saturated with sodium hydroxide, the upper oily layer of amine separated and further dried over sodium hydroxide and then over sodium. The amine was now distilled from sodium in a 250-cc. special Claisen flask. If the amine is properly dried there is very little forerun and no high boiling residue.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED OCTOBER 30, 1933

Inhibition of Oxidation of Phenylhydrazine

BY R. H. HAMILTON, JR.

In the course of a quantitative study of the osazone reaction, in which quantities of glucose of the order of magnitude of 10 mg. were used, it was necessary to find means of preventing tar formation. This end was attained by carrying out the reaction in sealed tubes from which all air had been evacuated.

It was later discovered that the presence of sodium bisulfite in the reaction mixture entirely prevented tar formation, even though air were present. A tube containing 1 mg. of glucose, 1 cc. of 50% acetic acid saturated with sodium acetate, 0.1 cc. of phenylhydrazine, 1 cc. of 50% $NaHSO_3$, and 8 cc. of water was heated for one hour in boiling water and cooled. The crystals separating were left in contact with the mother liquor for several months, the tube being stoppered to prevent evaporation. No discoloration of either crystals or mother liquor resulted, although a tarry precipitate quickly developed in a similarly prepared tube lacking the bisulfite.

LABORATORY OF PHYSIOLOGICAL CHEMISTRY
MEDICAL SCHOOL
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED NOVEMBER 13, 1933

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[1] Eastman Kodak Company Fellow, 1931–1932.

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. $CHCl_3$–RtOH
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 a, MeOH[a]	II, Leaf Xanthophyll b, $CHCl_3$–pet. ether	III, Lutein CH_2Cl_2–*n* heptane	IV, Lycopene[a] 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.

Acknowledgment is made to Professor W. H. Dore, of the University of California, with whom this work was performed.

CARNEGIE INSTITUTION OF WASHINGTON
DIVISION OF PLANT BIOLOGY
STANFORD UNIVERSITY, CAL.

RECEIVED NOVEMBER 20, 1933

[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**, 1959 (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
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MD.
RECEIVED NOVEMBER 29, 1933

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
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
RECEIVED DECEMBER 8, 1933

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