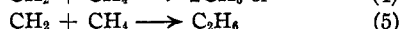
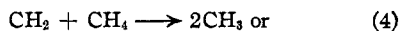


bines on the walls or disappears according to reaction (3) before reaching the mirror.

If on the other hand reaction (2) is the primary process it should be followed by



and these processes must each have an activation energy of less than 12 Cal. in order to account for the absence of methylene radicals. Since the reaction of the radicals with ether⁴ has an activation energy of approximately 15 Cal., the analogous reaction with methane probably has a higher activation energy and we feel therefore that reaction (1) probably represents the first step in the thermal decomposition of methane.

Summary

When methane is decomposed thermally in a

flowing system, methyl groups escape from the furnace and can be identified as dimethyl ditelluride. No telluroformaldehyde is formed, thus proving the absence of methylene radicals in the gases leaving the furnace. Furthermore, we did not detect any hydrides of tellurium in the liquid air trap, indicating the absence of atomic hydrogen among the fragments leaving the furnace.

Our experiments indicate that methane undergoes a primary dissociation into methyl groups and atomic hydrogen; the atomic hydrogen disappears before reaching the mirror, either on the walls or by reaction with methane to form methyl radicals and molecular hydrogen.

The activation energy of the primary process is 100 ± 6 Cal.

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[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Formation of Glycidamides by the Action of Hydrogen Peroxide on α,β -Ethylenic Nitriles¹

BY JAMES V. MURRAY AND JOHN B. CLOKE

In 1885, Radziszewski² described a method for the preparation of amides by the action of 3% hydrogen peroxide on nitriles in the presence of alkali and at a temperature of 40°. He formulated the reaction as: $\text{RCN} + 2\text{H}_2\text{O}_2 \longrightarrow \text{R}-\text{CO}-\text{NH}_2 + \text{H}_2\text{O} + \text{O}_2$. Since that time Deinert,³ Friedländer and Weisberg,⁴ Rupe and Majewski,⁵ Bogert and Hand,⁶ Keiser and McMaster,⁷ Dubsky,⁸ McMaster and Langreck,⁹ Oliveri-Mandalà¹⁰ and others have described modifications and extensions of the method.

In some work reported in 1932, Knowles and Cloke,¹¹ in connection with the proof of a nitrile structure, subjected α -phenylcrotononitrile, $\text{CH}_3\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CN}$ (I), to the Radziszewski reaction with the expectation of obtaining α -phenyl-

crotonamide, $\text{CH}_3\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CONH}_2$ (II). However, consistently low values for the nitrogen in the compound obtained, which were in harmony with the formula $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$, suggested that an oxidation had taken place, and when the substance was found to give methyl benzyl ketone, $\text{CH}_3\text{COCH}_2\text{C}_6\text{H}_5$, on acid hydrolysis, it was erroneously identified as α -phenylacetoacetamide, $\text{CH}_3\text{COCH}(\text{C}_6\text{H}_5)\text{CONH}_2$ (III). Later, however, a perusal of the work of Weitz and Scheffer¹² on the formation of ketoxido compounds from unsaturated ketones cast doubt on this structure (III) and suggested that the compound $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ was actually the isomeric α -phenyl- β -methylglycidamide, $\text{CH}_2-\underset{\text{O}}{\text{C}}(\text{C}_6\text{H}_5)\text{CONH}_2$ (IV), which

view was practically confirmed when it was found¹³ that the compound failed to give a color with ferric chloride. Finally the phenylacetoacetamide structure (III) was excluded definitely when it was found that two forms of this compound had already been prepared by Ogata and Ito¹⁴ by the hydrolysis of acetobenzyl cyanide,

(1) This paper has been abstracted from the second part of a thesis presented by James Vincent Murray, Jr., to the Rensselaer Polytechnic Institute in June, 1934, in partial fulfillment of the requirements for the degree of Chemical Engineer.

(2) Radziszewski, *Ber.*, **18**, 355 (1885).

(3) Deinert, *J. prakt. Chem.*, [2] **52**, 431 (1895).

(4) Friedländer and Weisberg, *Ber.*, **23**, 1841 (1895).

(5) Rupe and Majewski, *ibid.*, **33**, 3403 (1901).

(6) Bogert and Hand, *THIS JOURNAL*, **24**, 1034 (1902).

(7) Keiser and McMaster, *Am. Chem. J.*, **49**, 81 (1913).

(8) Dubsky, *J. prakt. Chem.*, [2] **93**, 137 (1916).

(9) McMaster and Langreck, *THIS JOURNAL*, **39**, 103 (1917).

(10) Oliveri-Mandalà, *Gazz. chim. ital.*, **52**, I, 107 (1922).

(11) Knowles and Cloke, *THIS JOURNAL*, **54**, 2028 (1932).

(12) Weitz and Scheffer, *Ber.*, **54B**, 2327 (1921).

(13) Green, "Thesis," Rensselaer Polytechnic Institute, 1933.

(14) Ogata and Ito, *J. Pharm. Soc. Japan*, No. **409**, 209-231 (1916).

$\text{CH}_3\text{COCH}(\text{C}_6\text{H}_5)\text{CN}$, with concentrated sulfuric acid, and that the properties of neither of their isomers corresponded with those of the compound $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$. By elimination, the oxido amide structure (IV) was clearly indicated.

The final analogical proof of the structure (IV) came as a result of the extension of the Radziszewski reaction, as modified by the writers, to α -phenylcinnamionitrile, $\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CN}$, which gave a 90% yield of α,β -diphenylglycidamide, $\text{C}_6\text{H}_5\text{CH}-\text{C}(\text{C}_6\text{H}_5)\text{CONH}_2$ (V), which fortu-

nately had already been prepared by Kohler and Brown¹⁵ starting with desyl chloride, $\text{C}_6\text{H}_5\text{CHClCOC}_6\text{H}_5$. That our compound is identical with that of Kohler and Brown follows from its melting point and from the fact that it can be transformed by suitable hydrolyses into their α,β -diphenyl- α,β -dihydroxypropionamide and α,β -diphenylglycidic acid.

Modification of the Radziszewski Amidation Reaction.—Since the Radziszewski reaction, even with the use of more concentrated hydrogen peroxide as suggested by McMaster and Langreck,⁹ failed to work well with our very insoluble nitriles, such solvents as methanol, ethanol and acetone were employed. Although the addition of any one of these solvents leads to the complete miscibility of the nitrile with the alkaline hydrogen peroxide solution, the acetone has given by far the best results. Thus in one comparative experiment, *o*-tolunitrile gave a 35% yield of *o*-toluamide in aqueous solution, a 52% yield in aqueous ethanol solution, and practically 100% of the amide in aqueous acetone solution. In another experiment the formation of a glycidamide in aqueous acetone progressed rapidly and gave a practically quantitative yield of the oxido amide, whereas that in a water-acetone-methanol solution, aqueous "methyl acetone," was quite sluggish, and even at the end of several days a considerable amount of the original nitrile was recovered.

Effect of Structure on Glycidamide Formation.—Not all α,β -ethylenic nitriles give glycidamides when they are subjected to the modified Radziszewski reaction. Thus Keiser and McMaster⁷ found that fumaronitrile reacts with hydrogen peroxide in alkaline solution to give fumaramide, and we have found that cinnamionitrile also gives the ordinary amide. Moreover, thus far acrylonitrile

has given only resinous products, and the true aromatic nitriles, such as *o*-tolunitrile, which in the light of the Kekulé formula might be regarded as α,β -ethylenic nitriles, appear to give the simple amides only.

In order to ascertain whether β,γ -ethylenic nitriles would also form oxido amides, allyl cyanide, $\text{CH}_2=\text{CHCH}_2\text{CN}$, was subjected to the Radziszewski reaction. In this case, however, an 80% yield of vinylacetamide was obtained. This evidence points to a 1,4 addition to the system, $\text{>C}=\text{C}-\text{C}\equiv\text{N}$, in the formation of the glycidamides, which is in harmony with the views of Weitz and Scheffer¹² on the formation of ketoxido compounds. Moreover, the simple amide does not appear to be an intermediate in the formation of the glycidamides from α,β -ethylenic nitriles, since no glycidamide was obtained from either α -phenylcrotonamide (II) or α -phenyl- β -*n*-propylacrylamide when these were subjected to the Radziszewski reaction.

Experimental Part

The Formation of α,β -Diphenylglycidamide from α -Phenylcinnamionitrile and Hydrogen Peroxide.—A mixture of 2 g. of α -phenylcinnamionitrile, prepared by the method of Meyer and Frost,¹⁶ and 25 cc. of 10% hydrogen peroxide was treated with enough acetone to bring about the miscibility of the nitrile with the aqueous solution. At this point 3 cc. of a 10% solution of sodium carbonate was added to this solution, which led at once to the evolution of oxygen and the generation of considerable heat and after a few minutes to the separation of a white crystalline precipitate. At the end of three days the mixture was poured into a crystallizing dish, the acetone was largely removed under diminished pressure, when the white crystals were collected on a filter and recrystallized from the minimum quantity of boiling water. The crystals which were dried under diminished pressure over phosphorus pentoxide melted at 203–204° (corr.), which agrees with the value reported by Kohler and Brown.¹⁵ A 90% yield of the compound was obtained.

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$: N, 5.86. Found: N, 5.88, 5.99.

In an initial run wherein the reaction was carried out at a higher temperature, the same oxido amide was obtained after six recrystallizations together with unchanged α -phenylcinnamionitrile and some other compound which was not identified.

The Action of Hydrogen Peroxide on Cinnamionitrile.—Cinnamionitrile¹⁷ in aqueous acetone was treated with hydrogen peroxide and sodium carbonate solution in the usual way. The compound formed, however, was cinnamamide and not the expected β -phenylglycidamide.

(16) Meyer and Frost, *Ann.*, **250**, 157 (1889).

(17) Reid and Van Epps, *This Journal*, **38**, 2125 (1916).

(15) Kohler and Brown, *This Journal*, **55**, 4299 (1933).

Anal. Calcd. for C_9H_9ON : N, 9.53. Found: N, 9.48, 9.31.

That the compound was cinnamamide was shown by its hydrolysis to cinnamic acid and also by the fact that its melting point ($147-148^\circ$ uncorr.) was unchanged when it was mixed with a known specimen of cinnamamide.

α -Phenyl- β -propylacrylonitrile.—A volume of 4 cc. of 20% sodium ethoxide was added gradually to a solution of 41 g. of phenylacetonitrile and 41 g. of freshly distilled *n*-butyraldehyde in 85 cc. of absolute alcohol, which was cooled to -10° , when the mixture was allowed to remain in a refrigerator for two weeks. At this stage the addition of 200 cc. of water to the mixture gave an oily precipitate which was washed twice with water, dissolved in ether, dried over anhydrous sodium sulfate and distilled. The redistillation of 36.5 g. of the fraction of b. p. $115-117^\circ$ at 3 mm. gave 32 g. of the nitrile of b. p. $118-118.5^\circ$ (corr.) at 3.5 mm., a 54% yield. The compound possessed a density d_4^{20} of 0.9725 and an index of refraction n_D^{20} of 1.54043, which correspond to a molecular refraction of 55.2.

Anal. Calcd. for $C_{12}H_{13}N$: N, 8.19. Found: N, 8.25, 8.29.

α -Phenyl- β -*n*-propylacrylamide.—A solution of 2 g. of α -phenyl- β -*n*-propylacrylonitrile in 10 g. of concentrated sulfuric acid was allowed to stand for three days when it was poured into 100 cc. of ice water. The mixture was extracted with ether, the ether solution was allowed to evaporate and the residue of amide and nitrile was extracted with petroleum ether, whereby the nitrile was removed. The recrystallization of the residue from boiling water gave a mass of fine white crystals of m. p. $139-140^\circ$ (corr.).

Anal. Calcd. for $C_{12}H_{15}ON$: N, 7.41. Found: N, 7.38, 7.50.

The Action of Hydrogen Peroxide on α -Phenyl- β -propylacrylonitrile.—The action of hydrogen peroxide on α -phenyl- β -propylacrylonitrile in aqueous acetone-carbonate solution gave a mass of white prismatic needles of m. p. $145-146^\circ$ (corr.).

Anal. Calcd. for $C_{12}H_{15}O_2N$: N, 6.83. Found: N, 6.97, 6.92.

The foregoing compound whose nitrogen analysis agreed with the α -phenyl- β -propylglycidamide structure was distinct from the α -phenyl- β -propylacrylamide as shown by a mixed melting point determination. It was very resistant

to attack by alcoholic potassium hydroxide, but it gave a brownish oil when it was refluxed with concentrated hydrochloric acid for several hours. However, no semicarbazone was obtained from the oil, and lack of material precluded further work.

Action of Hydrogen Peroxide on Allyl Cyanide.—The action of hydrogen peroxide on 2 g. of allyl cyanide in aqueous acetone gave an 80% yield of glistening plates of m. p. $72-72.5^\circ$, which corresponds to the melting point of vinylacetamide prepared by Brulé¹⁸ by a different method.

Anal. Calcd. for C_4H_7ON : N, 16.5. Found: N, 16.7, 16.6.

Summary

1. α -Phenylcrotonitrile reacts with hydrogen peroxide in the presence of sodium carbonate and aqueous acetone to give a nearly quantitative yield of α -phenyl- β -methylglycidamide instead of α -phenylacetoacetamide as previously reported by Knowles and Cloke. Similarly, α -phenylcinnamitrile gives α,β -diphenylglycidamide, which has been prepared by another method by Kohler and Brown.

2. Not all α,β -ethylenic nitriles give glycidamides with hydrogen peroxide, since cinnamitrile yields cinnamamide.

3. The formation of oxido amides by the hydrogen peroxide reaction appears to be restricted to those nitriles possessing the group $\text{>C=C-C}\equiv\text{N}$, since allyl cyanide gives the ordinary amide, and α -phenylcrotonamide and α -phenyl- β -*n*-propylacrylamide are not attacked by the peroxide.

4. α -Phenyl- β -*n*-propylacrylonitrile is described.

Future papers will consider the mechanism of the Radziszewski reaction and its use for the identification of various types of nitriles.

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(18) Brulé, *Bull. soc. chim.*, [iv] 5, 1019-22 (1909).