$$(HNC(NH_2)_2)_2 \cdot H_2CO_3 + (SCSN_3)_2 \longrightarrow$$
$$HNC(NH_2)_2 \cdot HSCSN_3 + HNC(NH_2)_2 \cdot HOSCSN_3 + CO_2$$

The very unstable oxy-azido-dithiocarbonate quickly decomposes, with evolution of two-thirds of its azide nitrogen as gas (or one-third of the total nitrogen of the original azido-carbondisulfide used), deposition of sulfur and formation of the oxy-thiocyanate. This would tend to form the tri-oxy-thiocyanate, or chlorate analog.[5]

The guanidine azido-dithiocarbonate, on long standing, decomposes quantitatively, yielding nitrogen, sulfur and the thiocyanate. Five-sixths of the total original azido-dithiocarbonate is therefore converted into thiocyanate, while the remaining sixth yields the chlorate analog, guanidine tri-oxy-thiocyanate, or cyanosulfate, which hydrolyzes into the sulfate and cyanide.[5]

The amount of free sulfur recovered in this experiment corresponds to a yield of about 94% of the theoretical, while the guanidine thiocyanate, without correction for the amount unavoidably left in the mother liquor, corresponds to a yield of 83%. Nitrometric experiments upon samples of one-tenth the weight previously used led to the conclusion that two atoms of nitrogen gas per mole of $(SCSN_3)_2$, or one-third of the total azide nitrogen, were liberated at once. This confirms the theory that the oxy-azido-dithiocarbonate undergoes very rapid decomposition under the prevailing conditions.

Summary

Guanidine trinitride, $HNC(NH_2)_2 \cdot HN_3$ (m. p. 93.5°), has been prepared by interaction, in aqueous solution, of (1) guanidine hydrochloride and silver trinitride, (2) guanidine sulfate and barium trinitride, and (3) guanidine carbonate and hydronitric acid.

Guanidine azido-dithiocarbonate, $HNC(NH_2)_2 \cdot HSCSN_3$ (dec. 88–90°), has been prepared by interaction in aqueous solution of (1) guanidine carbonate and azido-dithiocarbonic acid, and (2) guanidine trinitride and carbon disulfide.

Certain physical properties and chemical reactions of these salts have been studied, and a preliminary investigation of the reaction between guanidine carbonate and the free halogenoid, azido-carbondisulfide, has been made.

ITHACA, N. Y. RECEIVED AUGUST 28, 1934

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(5) Söderbäck, *Ann.*, **419**, 217 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XI. The Methylene Radical

BY F. O. RICE AND A. L. GLASEBROOK[1]

In this paper we shall describe some experiments in which we have proved that under certain conditions the methylene radical can be prepared by the thermal decomposition of diazomethane. When this compound is carried in a current of ether or butane at low pressures and is decomposed[2] at temperatures below about 550°, the fragments produced readily remove mirrors of tellurium, selenium, antimony and arsenic whereas zinc, cadmium, thallium, lead and bismuth mirrors are not removed.[3] We analyzed the product formed by the combination of the fragments with metallic tellurium and found it to be a polymer of telluroformaldehyde $(HCHTe)_n$; this is a red involatile solid which deposits on the walls of the tube just beyond the tellurium mirror Since methyl groups combine with metallic tellurium to form a red liquid, dimethyl ditelluride $CH_3TeTeCH_3$, which passes over into the liquid air trap, it is very easy to distinguish between the two radicals. We found the methylene group to be extremely reactive and to have a half life of the same order as that of the alkyl radicals, namely, of only a few thousandths of a second. It can be carried in a current of ether or butane under our conditions up to 600°; above this temperature but below the decomposition point of the carrier gas it disappears and is replaced by methyl groups.

Experimental

We have already pointed out that those metals which react with methyl radicals may be divided into two groups, one of which reacts with the methylene radical and the other not. We examined this effect in a more quantita-

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[1] General Motors Co. Fellow, 1930–1934.

[2] A full description of the technique used is given in a paper by Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932). See also Rice and Glasebrook, *ibid*., **55**, 4329 (1933), for a preliminary account of this work.

[3] Methyl radicals readily react with all these metals.

tive manner using tellurium and zinc as representative metals of the two groups. Standard zinc mirrors were deposited 1 cm. from the end of the furnace and the time required for their removal when pure ether was passed through the furnace at different temperatures was noted. The results (curve 1) are shown in Fig. 1. The experiment was repeated using a mixture of diazomethane and ether in the furnace, and curve 2, Fig. 1, was obtained, showing that the presence of the diazomethane has only a very slight effect on the time of removal of standard zinc mirrors by ether. We then repeated the two foregoing experiments using tellurium mirrors, and obtained curves 3 and 4. It is clear that there is some molecular fragment produced at low temperatures which removes a tellurium mirror but not one of zinc. When these experiments were repeated with standard mirrors of cadmium and antimony, substantially the same results were obtained: removal of the cadmium mirrors with the furnace below 750° was exceedingly slow both with ether alone and with ether mixed with diazomethane. On the other hand, using antimony mirrors, the ether–diazomethane mixture removed the mirrors at temperatures as low as 500°, whereas ether alone caused exceedingly slow removal even at 750°. We also carried out another series of experiments using tellurium mirrors with butane as the carrier gas for the diazomethane and obtained substantially the same results as when ether was used.

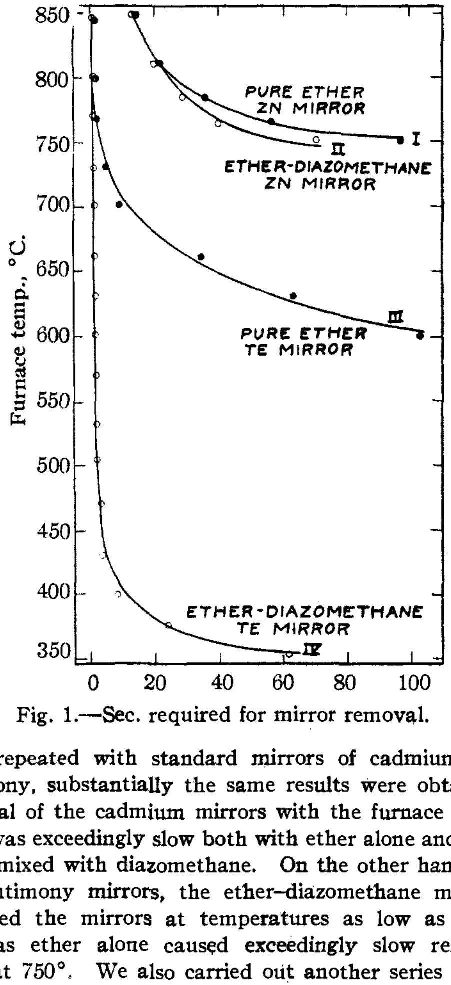

Fig. 1.—Sec. required for mirror removal.

We next undertook to identify the fragments formed during the decomposition of diazomethane at different temperatures. When ether or butane is decomposed and the fragments passed over metallic tellurium, a red liquid, dimethyl ditelluride, $CH_3TeTeCH_3$, is formed and passes over into the liquid air trap.[4] This same compound is formed when diazomethane is mixed with the ether or butane, provided the furnace temperature is not less than 700°. Since the dimethyl ditelluride is the only compound that is formed, only methyl groups can have issued from the furnace.[5]

On the other hand, if the decomposition of the diazomethane (carried in a current of ether or butane) is performed at 500° or lower, quite different results are obtained. Using the fragments to remove tellurium mirrors it is found that no dimethyl ditelluride is formed; instead of the usual red liquid which is carried in the stream of gas to the liquid air trap, a deep red solid deposits on the tube just beyond the tellurium mirrors. This compound is so involatile that it cannot be driven down the tube without decomposition. We obtained a sample by subliming it from the walls of the tube, at 100° and in a high vacuum, onto a cooled smaller concentric tube which could then be withdrawn from the apparatus. We found the compound to be stable in the air, decomposing at about 150° to give metallic tellurium. It is insoluble in water and unlike dimethyl ditelluride, it is also quite insoluble in alcohol, ether and benzene. Analysis of a sample carefully distilled free of metallic tellurium gave C, 8.28, and H_2. 1.33. The theoretical values for the compound telluro-formaldehyde are C, 8.40, and H_2, 1.41. We have concluded therefore that the compound formed when diazomethane is decomposed below 500° in a current of ether and the fragments are allowed to react with tellurium, is a polymer of telluroformaldehyde, $(CH_2Te)_n$; owing to its involatility and insolubility we were unable to determine the molecular weight of the substance.[6]

This substance does not seem to have been described previously. Morgan and Drew[7] mention the formation of ditelluromethane, $(CH_2Te_2)_n$, a red amorphous insoluble powder which changes rapidly to a black modification above 30°; however, we obtained no evidence of the formation of this compound in any of our experiments. The compound mentioned by Belchetz[8] as occurring in the liquid air trap after the fragments from methane had passed over a tellurium mirror cannot be telluroformaldehyde because the latter compound is far too involatile to travel from the tellurium mirror to the liquid air trap.

Discussion

This experimental work is not in agreement with current ideas on the nature of the methylene radi-

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[4] Rice and Glasebrook, This Journal, **56**, 2472 (1934).

[5] Furthermore, when diazomethane is decomposed in a current of ether, and the fragments brought in contact with metallic mercury, no organo-mercuric compound is formed when the furnace temperature is below 650°. On raising the temperature to 700°, however (at which temperature ether alone does not decompose), and adding iodine to the contents of the liquid air trap after distilling off the undecomposed diazomethane, methyl mercuric iodide can be identified as the main product, proving conclusively that methyl groups are formed when diazomethane is decomposed above 700° (see Rice and Glasebrook, This Journal, **55**, 4329 (1933)).

[6] We also made some unsuccessful attempts to detect the formation of the methylene radical by combining it with carbon monoxide to give ketene; also by passing it over "mirrors" of different dyes which might be expected to change color on methylation. Paneth, *Trans. Faraday Soc.*, **30**, 89 (1934), mentions that he was unable to detect any methyl benzoate when the methylene radical was passed over benzoic acid.

[7] Morgan and Drew, *J. Chem. Soc.*, **127**, 531 (1925).

[8] Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

cal,[9] most of which are based on Nef's[10] premise that organic compounds readily undergo a primary decomposition into a stable smaller molecule and a radical containing bivalent carbon.[11] The decomposition of methane recently has been interpreted according to this scheme of primary alkylidene formation, $CH_4 \longrightarrow CH_2 + H_2$, and it was found that the observed kinetics of the methane decomposition agree with a scheme based on this as its primary reaction.[9b] Furthermore, recent calculations appear to show that bivalent carbon is formed very easily; for example, according to Mecke,[9a] the energy required to dissociate CH_3 to CH_2 is only 25 Cal. and Norrish[9c] has concluded from various considerations that the CH_2 radical should be formed easily from CH_3 and that it should have a peculiar stability resembling that of a molecule rather than of a free radical.

Furthermore, this experimental work[12] is not in agreement with the experimental results of Belchetz, who decomposed methane on a hot platinum filament and reported that the methylene radical was identified. Telluroformaldehyde, the product of the combination of methylene radicals and tellurium, is too involatile to pass over into the liquid air trap and if it had been formed would have been deposited on the walls of the apparatus just beyond the tellurium mirror.

It seems clear from our results that the methylene radical is a highly reactive fragment of short life that cannot be prepared by the thermal decomposition of methane, ethane and propane in the temperature range 800–1100°, since only methyl groups can be detected among the fragments produced in the thermal decomposition of these compounds.[13]

We have attempted to calculate the number of collisions which an original methylene group underwent in the furnace at the higher temperature, when only methyl groups were identified among the products, but owing to the conditions of our flow experiments our calculations are not very accurate. However, a value of 15 ± 5 Cal. for the activation energy of the reaction of methylene radicals with ether is consistent with our results, indicating that the methylene group is extremely reactive and readily removes hydrogen atoms from surrounding molecules, to form the more stable methyl groups. Our experiments all seem to show that the methyl radical is stable with respect to methylene even up to temperatures of 1000°; also that the half-life of the methylene group is of the same order as that of the alkyl radicals, namely, only a few thousandths of a second.

Summary

1. Our experiments have shown that the free methylene group is formed when diazomethane is decomposed below 500° in a current of ether or butane.

2. When this decomposition is carried out above 650° but below the decomposition point of ether, only methyl groups issue from the furnace.

3. The methylene group reacts with certain metals, namely, with tellurium, selenium, arsenic and antimony, and not at all with certain other metals. In this latter group are zinc, cadmium, mercury, thallium, lead and bismuth. The methyl group, on the other hand, reacts with all of the metals listed, thus affording a simple and conclusive test as to whether methyl or methylene groups have been formed in any experiment.

4. When methylene groups react with tellurium a characteristic compound which is a polymer of telluro-formaldehyde, $(CH_2Te)_n$, is formed. This is a red solid, with a very low vapor pressure, insoluble in the usual organic solvents. Since methyl groups react with tellurium to form a quite different compound, dimethyl ditelluride, $CH_3TeTeCH_3$, a further method of differentiation between methylene and methyl groups is available.

BALTIMORE, MARYLAND

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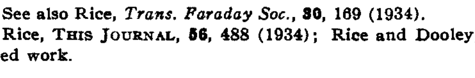
[9] (a) Mecke, *Z. Elektrochem.*, **36**, 589 (1930); (b) Kassel, THIS JOURNAL, **54**, 3949 (1932); (c) Norrish, *Trans. Faraday Soc.*, **30**, 108 (1934); (d) Belchetz, *ibid.*, **30**, 170 (1934).

[10] Nef. *Ann.*, **298**, 202 (1897).

[11] For example, the thermal decomposition of ethane or ethyl chloride would be represented as involving the primary formation of the ethylidene radical: $C_2H_6 \longrightarrow CH_3CH + H_2$, or $CH_3CH_2Cl \longrightarrow CH_3CH + HCl$. This radical was then supposed to rearrange as follows:



$$\underset{\displaystyle H}{\underset{|}{CH_2}}—CH \longrightarrow \underset{|}{CH_2}—\underset{|}{CH_2} \longrightarrow CH_2{=}CH_2.$$

[12] See also Rice, *Trans. Faraday Soc.*, **30**, 169 (1934).

[13] Rice, THIS JOURNAL, **56**, 488 (1934); Rice and Dooley, unpublished work.