preliminary oxidation. It is also possible that the rate of burn of a charge fired by a spark may depend upon factors similar to those which govern the low temperature oxidation. The problem is extremely complicated and the authors do not feel that the data presented in this paper give by any means the complete account of engine detonation. Nevertheless, they represent an interesting correlation of laboratory data with engine operation, and are presented with the hope that they may contribute to clearing up at least certain phases of this important problem.

VII. Summary

1. Experimental data have been presented on the vapor phase oxidation of *n*-octane and *n*-heptaldehyde in the presence of tetra-ethyl lead.
2. The effect of tetra-ethyl lead seems to be chiefly that of slowing down the oxidation of aldehydes to carbon monoxide, water and other aldehydes.
3. The data, combined with those of Parts I and II, are discussed in comparison with the behavior of the hydrocarbons as fuel in the internal combustion engine, and certain correlations are pointed out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE ACTION OF PHENYL ISOCYANATE ON URETHANS, UREAS AND THIOUREAS

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Phenyl isocyanate, which was first obtained by A. W. Hofmann,[2] is characterized by its ability to form addition products with the N=C double bonding. Thus with alcohols urethans, $C_6H_5NHCOOR$, are formed while with ammonia and with primary and secondary amines, substituted ureas result. The presence of aryl groups in the secondary amines often tends to slow up or even in some cases to prevent the expected addition, $RR'NH + C_6H_5NCO = C_6H_5NHCONRR'$.

Since the nature of the hydrocarbon (aryl) group has been found to affect the course of the reaction, it seemed worth while to study the reactivity of phenyl isocyanate toward the group $RNH(NH_2)$ when it was linked with a CO or CS complex, in order to determine their influence upon the expected additions.

In the present investigation the compounds chosen were urethans, ureas and thioureas where the primary reaction might be expected to yield (a)

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[1] From a dissertation presented by Hans Lakra to the Faculty of the Graduate School of the University of Kansas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hofmann, *Ann.*, **74**, 9 (1850); *Ber.*, **3**, 655 (1870).

with urethans, allophanic esters, $C_6H_5NHCONHCOOR$; with ureas, biurets, $C_6H_5NHCONHCONH_2$, and with thioureas, monothiobiurets, $C_6H_5NHCONHCSNH_2$, or their substitution products where an H had been replaced by aryl or alkyl groups.

Such addition products were isolated in a number of cases; in others only the dissociation products of the initial compound. Any simple formulation of the results was rendered difficult in many instances by the fact that one of the dissociation products was isocyanic acid, which could then condense with itself to form isocyanuric acid or with amino compounds, yielding ureas or biurets. Higher temperatures favored this latter type of reaction.[3]

Experimental

Phenyl Isocyanate and Urethan.—Molecular proportions of the two reagents were heated at 140–160° for six hours.[4] From the reaction product were isolated: (1) phenyl allophanic ester, $C_6H_5NHCONHCOOC_2H_5$; (2) phenylurethan, $C_6H_5NHCOOC_2H_5$; (3) phenylisocyanuric acid, $C_6H_5H_2C_3O_3N_3$; and (4) phenylcarbethoxybiuret, $C_6H_5NHCONHCONHCOOC_2H_5$. No. 1 is formed by direct addition; Nos. 2 and 3 by dissociation of the urethan into HNCO and alcohol and subsequent addition of alcohol or the dimer $(HNCO)_2$ to the isocyanate, while in No. 4 the phenylisocyanate and alcohol add to $(HNCO)_2$. No evidence was obtained as to the intermediate possible formation of allophanic ester which with the isocyanate would yield the carbethoxybiuret.

Phenyl Isocyanate and Phenylurethan.—Heated at 150° a little carbanilide is formed.[5] At temperatures from 200–250° this is the main product. While the phenylurethan would account for part of the carbanilide, the increased amount would indicate that the ethyl alcohol from the urethan loses a mole of water which then reacts with additional isocyanate to form diphenylurea.[6]

Phenyl Isocyanate and Ethylurethan, $C_2H_5NHCOOC_2H_5$.—The mixture was heated at 175° for six hours. The only product isolated was diphenylurea. No ethylphenylurea or diethylurea was detected due to the volatility of the dissociation products, ethylamine and ethyl isocyanate.

Phenyl Isocyanate and Allophanic Ester.—The two compounds failed to react at 125°. At 160° unchanged allophanic ester, carbanilide and isocyanuric acid were isolated.

Anal. Calcd. for $C_3H_3N_3O_3$: N, 32.55. Found: N, 32.13.

Heated at 170–178° an additional product, phenylisocyanuric acid was obtained.

Anal. Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.10.

Allophanic ester alone slowly decomposes at 160°, yielding ammonia and isocyanuric acid. The carbanilide is due to the intermediate formation of phenylurea ($C_6H_5NCO + NH_3$) and the phenylisocyanuric acid is formed as indicated in the case of urethan.

Phenyl Isocyanate and Urea.—After heating at water-bath temperature for seven hours, there was isolated a little diphenylurea, and unchanged urea, but the main

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[3] This work harmonizes with the results on "Urea Dearrangement," Davis and Underwood, THIS JOURNAL, **44**, 2595 (1922); Davis and Blanchard, *ibid.*, **45**, 1816 (1923).

[4] Dains, Greider and Kidwell, *ibid.*, **41**, 1008 (1919).

[5] Schiff, *Ber.*, **3**, 249 (1870).

[6] Dains, THIS JOURNAL, **21**, 180 (1899).

product was α-monophenylbiuret, $C_6H_5NHCONHCONH_2$, formed by simple addition. This, after recrystallization from hot water and from dilute alcohol, melted at 156–157°.[7]

Anal. Calcd. for $C_8H_9N_3O_2$: N, 23.48. Found: N, 23.60, 23.27.

Phenyl Isocyanate and Urea at 120° for Four Hours.—In this case the following products were isolated and identified: ammonia, unchanged urea, biuret,[8] diphenylurea, monophenylurea, phenylisocyanuric acid[9] and isocyanuric acid.

The results are in harmony with what might be predicted from a mixture containing phenyl isocyanate, urea, ammonia and isocyanic acid ($NH_2CONH_2 \rightleftharpoons NH_3 + HNCO$).

$$2C_6H_5NCO + 2NH_3 = 2C_6H_5NHCONH_2 = (C_6H_5NH)_2CO + NH_2CONH_2$$
$$NH_2CONH_2 + HNCO = NH(CONH_2)_2$$
$$3HNCO = C_3H_3N_3O_3$$
$$C_6H_5NCO + 2HNCO = C_6H_5H_2C_3N_3O_3$$

Results When Heated at 140° for Seven Hours.—The main product was carbanilide. No biuret or monophenylurea was isolated.

Acyl Substituted Ureas.—Phenyl isocyanate and acetylurea failed to react at water-bath temperature, but heated at 130 or 160° for five hours, the same products were obtained, *viz.*, α-acetyl-β-phenylurea and isocyanuric acid. The results could be due either to the action of the isocyanate upon acetamide, ($CH_3CONHCONH_2 \rightleftharpoons CH_3CONH_2 + HNCO$), or addition to the acetylurea, as follows: $CH_3CON(CONHC_6H_5)CONH_2$ and then loss of HNCO.

The fact that no phenylisocyanuric acid was detected is in favor of this latter formulation.

In the same way benzoylurea and the isocyanate yielded at 150° benzoylphenylurea, which at 210° slowly dissociated into phenylisocyanate and benzamide (m. p. 128°).

Phenyl Isocyanate and Monophenylurea.—Kuhn and Henschel digested the above mixture[10] at 120° and reported the formation of 1,5-diphenylbiuret and traces of a higher-melting product. On repeating their work but only heating at 100° for four hours, there was obtained diphenylurea, 1,5-diphenylbiuret,[11] m. p. 210°, and monophenylbiuret, m. p. 156–157°, confirmed by a mixed melting point with a known sample of monophenylbiuret.

The result would seem to indicate that the isocyanate can add to the phenylurea at two points; first at Position 3, yielding the 1,5-diphenylbiuret, and at Position 1, giving the isomeric biuret, $C_6H_5NHCON(C_6H_5)CONH_2$. This dissociates into diphenylurea and isocyanic acid, which then adds to the unchanged phenylurea. The same products would be formed if it were assumed that some of the phenylurea dissociated, $C_6H_5NHCONH_2 = C_6H_5NH_2 + HNCO$, but this seems a question at 100°.

The fact that phenylurea when boiled for several hours with water yields aniline can well be regarded as a simple case of hydrolysis.[12]

Disubstituted Ureas.—Carbanilide and phenyl isocyanate at 150° gave 1,3,5-triphenylbiuret (m. p. 147°).[13] Above its melting point the biuret is unstable, breaking down into carbanilide and the isocyanate.

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[7] Piccard and Carter, *J. Chem. Soc.*, **79**, 846 (1900); **81**, 1563 (1902); McKee, *Am. Chem. J.*, **26**, 254 (1901); Dains and Wertheim, THIS JOURNAL, **42**, 2307 (1920); Gatewood, *ibid.*, **47**, 407 (1925).

[8] *Anal.* Calcd. for $C_2H_5N_3O_2$: N, 40.79. Found: N, 40.53, 40.46.

[9] *Anal.* Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.23.

[10] Kuhn and Henschel, *Ber.*, **21**, 504 (1888).

[11] *Anal.* Calcd. for $C_{14}H_{13}N_3O_2$: N, 16.47. Found: N, 16.34.

[12] Davis and Blanchard, THIS JOURNAL, **45**, 1818 (1923).

[13] Hofmann, *Ber.*, **4**, 250 (1871); Kuhn and Henschel, *Ber.*, **21**, 504 (1888).

Anal. Calcd. for $C_{20}H_{17}N_3O_2$: N, 12.68. Found: N, 16.34.

Methylphenylurea and phenyl isocyanate failed to react at 100° but at 135–140° carbanilide alone was obtained, the probable intermediate 1,3-diphenyl-5-methylbiuret not being stable at this temperature.

Phenylacetylurea does not combine with the isocyanate at 150°, but at 200° diphenylurea is the main product. The acetylurea dissociates at this temperature into phenylisocyanate and acetamide; loss of a mole of water converts the isocyanate into diphenylurea.

Phenyl Isocyanate and Thiourea

1-Phenyl-4-thiobiuret, $C_6H_5NHCONHCSNH_2$.—This was formed in good yield when the two substances were heated at water-bath temperature for five hours. The residue was washed with dry ether and recrystallized from alcohol. It then melted at 186°.

Anal. Calcd. for $C_8H_9N_3OS$: N, 21.55. Found: N, 21.78, 21.67.

Its constitution was proved by the fact that on desulfurization with lead hydroxide in alcohol solution, α-monophenylbiuret was obtained. At 110° the thiourea and isocyanate yielded the same biuret mixed with carbanilide, the amount of which increased with rising temperature.

1-Phenyl-4-methylthiobiuret, $C_6H_5NHCONHC(CH_3)=NH$.—When the thiobiuret was heated with methyl iodide in a sealed tube in the water-bath, the hydrogen iodide salt was formed. Alkali precipitated from its water solution the free base, which when crystallized from alcohol melted at 147–8°.

Anal. Calcd. for $C_9H_{11}N_3OS$: N, 20.10. Found: N, 20.00, 20.19.

Mono- and Di-substituted Thioureas.—In no case was it possible to isolate addition products from the mono- and disubstituted thioureas. The sole products identified were diphenylurea and mustard oils. Thus allylthiourea and phenylthiourea reacted slowly at water-bath temperature, completely at 110–120°, yielding carbanilide and allyl- or phenylisothiocyanate, while allylphenylthiourea or diphenylthiourea at 120–130° gave quantitatively diphenylurea and allyl- or phenylisothiocyanate.[14]

Addition of Phenyl Isocyanate to the Isothiourea Ethers

Methylthiocarbonyldiphenyldiurea, $C_6H_5NHCON=C(SCH_3)NHCONHC_6H_5$.—The methyl iodide addition product of thiourea (22 g.) was dissolved in as little water as possible. To this was added phenyl isocyanate (24 g.) and a concentrated solution of potassium hydroxide (5–6 g.). On shaking a viscous mass was formed which slowly solidified. Purified from alcohol, it melted at 142°.

Anal. Calcd. for $C_{16}H_{16}N_4O_2S$: N, 17.07. Found: N, 16.82, 16.78. *Mol. wt.* in acetic acid: calcd., 328. Found: 289.

The same compound (m. p. 142°) was obtained from 1-phenyl-4-methylthiobiuret and the isocyanate.

The thio-ether was warmed for a few minutes with one mole of alcoholic potassium hydroxide, hoping thus to obtain the carbonyldiphenyldiurea. Instead the ether broke down into mercaptan, aniline and a product soluble in alkali which proved to be phenylisocyanuric acid.

Anal. Calcd. for $C_9H_7N_3O_3$: N, 20.48. Found: N, 20.19.

When the thio-ether was treated with potassium sulfhydrate, mercaptan was

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[14] Goldschmidt and Meissler, *Ber.*, **23**, 273 (1890).

eliminated with the formation of thiocarbonyldiphenyldiurea, $CS(NHCONHC_6H_5)_2$; m. p. 202°.[15]

The Ethyl Ether of Thiocarbonyldiphenyl-diurea, $C_6H_5NHCONHC(SC_2H_5)=NCONHC_6H_5$.—This was prepared from γ-ethylthiourea and phenyl isocyanate. Crystallized from 50% alcohol it melted at 145°.

Anal. Calcd. for $C_{17}H_{18}N_4O_2S$: N, 16.37. Found: N, 16.87.

Phenyl Isocyanate and the Methyl Ether of Phenylthiourea.—The two compounds united with the development of heat and gave 1,5-diphenyl-4-methylthiobiuret, $C_6H_5NHCON=C(SCH_3)NHC_6H_5$, melting at 108°.

Anal. Calcd. for $C_{15}H_{15}N_3OS$: N, 14.73. Found: N, 14.94.

The methyl thio-ether when treated with KSH yielded the corresponding 1,5-diphenyl-mono-thiobiuret, $C_6H_5NHCONHCSNHC_6H_5$, melting at 161°.

As shown by Johnson[16] and confirmed by our work, γ-methylthiourea combined with only one mole of phenyl mustard oil, yielding 1-phenyl-2-thio-4-methylthiobiuret (m. p. 122°).

These thio-ethers exhibit an interesting analogy to the corresponding oxygen isourea ethers in that both types add one mole of phenyl isothiocyanate and two moles of the phenyl isocyanate.[17]

Phenyl Isocyanate and the Ethyl Ether of Diphenylthiourea, $C_6H_5NHC(SC_2H_5)NC_6H_5$.—While no action was observed at 100°, two varying sets of results were obtained at higher temperatures. Thus the isocyanate (24 g.) and the thio-ether (52 g.) heated at 160–170° for three hours gave diphenylurea, phenyl mustard oil and triphenylcyanuric acid (m. p. 270°). Evidently in this case a portion of the isocyanate had condensed to the cyanuric acid and it is possible that the expected addition product, $C_6H_5NHCONC_6H_5C(SC_2H_5)NC_6H_5$, has broken down into carbanilide, phenyl mustard oil and ethylene, although this latter was not identified.

After heating in a sealed tube at 200°, the tube opened with pressure and the issuing gases had the odor of mercaptan. The reaction product consisted of diphenylurea and a thick oil soluble in ether which after distillation in a vacuum and crystallization from alcohol melted at 162°. It gave no test for sulfur and gave figures on analysis corresponding to carbodiphenylimide, $(C_6H_5N)_2C$.

Anal. Calcd. for $C_{13}H_{10}N_2$: N, 14.43. Found: N, 14.28.

No mustard oil or triphenylcyanuric acid was found. Evidently at 200° much of the thio-ether dissociated directly into mercaptan and carbodi-imide, a reaction which has been previously observed.

Guanidine Carbonate and Phenyl Isocyanate

The Diphenylamide of Guanidine Dicarboxylic Acid, $HN=C(NHCONHC_6H_5)_2$.—Michael[18] had obtained this compound by the action of the isocyanate on the guanidine carbonate and sodium ethylate. It was found that potassium hydroxide could be used with good results instead of the ethylate in concd. water solution. It melted at 174°.

Anal. Calcd. for $C_{15}H_{15}N_5O_2$: N, 23.57. Found: N, 23.82.

Action on Hydrolysis.—The diamide when refluxed for thirty minutes with 15% isodium hydroxide solution gave ammonia, aniline, diphenylurea and isocyanuric acid.

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[15] Unpublished investigation by John F. Olin, who has found that KSH hydrolyzes isothiourea ethers to the corresponding thio carbonylcompounds.

[16] Johnson, *Am. Chem. J.*, **29**, 482, 490 (1903); **30**, 172 (1903).

[17] McKee, *Am. Chem. J.*, **26**, 233 (1901); Bruce, THIS JOURNAL, **26**, 448 (1903).

[18] Michael, *J. prakt. Chem.*, [2] **49**, 42 (1904).

Anal. Calcd. for $C_3H_3N_3O_3$: N, 32.56. Found: N, 32.40.

When heated alone at 190–200° for three hours, ammonia, diphenylurea and isocyanuric acid were identified as decomposition products.

The observation was confirmed that guanidine unites with only one mole of phenyl isothiocyanate.[19] Its behavior in this respect is analogous to the isourea and isothiourea ethers.

Summary

1. Direct addition products of phenyl isocyanate were obtained with the following: urethan, urea, mono- and diphenylurea, thiourea and all isothiourea ethers containing a free NH grouping.
2. In all other cases, the results obtained were due (a) either to addition and subsequent breaking down of the addition product or (b) dissociation at the elevated temperature of the urethan, urea, etc., as

$$C_6H_5NHCONH_2 \rightleftharpoons C_6H_5NCO + NH_3 \rightleftharpoons C_6H_5NH_2 + HNCO$$
$$NH_2CONH_2 \rightleftharpoons NH_3 + HNCO$$
$$C_6H_5NHCOOC_2H_5 \rightleftharpoons C_6H_5NCO + HOC_2H_5$$

and the re-uniting of phenyl isocyanate and these fission products in various ways. This is illustrated especially by the formation of isocyanuric acid and its derivatives.

3. Thiourea ethers, isothiourea ethers and guanidine unite with two moles of phenyl isocyanate but with only one mole of phenyl isothiocyanate.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE POLARIMETRY SECTION, BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XIX. IMPROVEMENTS IN THE PREPARATION OF ALDONIC ACIDS[1]

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Introduction

It is customary to prepare an aldonic acid by the oxidation of the corresponding aldose with bromine water. The reaction is a slow one because of the retarding influence of the hydrobromic acid that is produced during its course.[2] If the aldose is not a monosaccharide it may be partly hydrolyzed by the hydrobromic acid, with a resulting poor yield of the desired acid. Thus Fischer and Meyer's[3] oxidations of lactose and maltose to their

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[19] Bamberger, *Ber.*, **13**, 1581 (1880).

[1] Publication approved by the Director of the Bureau of Standards. No. XVIII, Phelps and Hudson, THIS JOURNAL, **50**, 2049 (1928).

[2] Bunzel and Mathews, THIS JOURNAL, **31**, 464 (1909); Bunzel, *J. Biol. Chem.*, **7**, 157 (1910).

[3] Fischer and Meyer, *Ber.*, **22**, 361, 1941 (1889).