we find that n-pentane and n-butane have the approximate values 12 and 15 kcal., respectively. As an approximation to the truth, we may assume that these molecules are adsorbed with their major axes lying in the plane of the adsorbing surface and that the contribution to the heat of van der Waals adsorption is approximately 3 kcal. per $-CH_2$ group thus accounting for the difference of 3 kcal. between the C_4 and C_5, and for total contributions of 12 and 15 kcal. for the two hydrocarbons respectively at 0.05 coverage.

If one builds Hirschfelder three-dimensional molecular models of n-pentane and neopentane it is apparent that the n-pentane could be so placed on a plane surface as to bring all its $-CH_2$ or $-CH_3$ groups into close contact. On the other hand, in the case of the neopentane, three $-CH_3$ groups could make close contact with the surface; the central carbon atom would be near enough to make some contribution to the total attraction between the surface and the adsorbed molecule, but the fourth $-CH_2$ group would be so far removed from the surface as to make relatively little contribution to the van der Waals forces, since such forces are inversely proportional approximately to the cube of the distance of the group from the surface. While it is obviously naive to assume that the surface is truly planar from the point of view of the adsorbate molecule, yet the molecular configurations of n-pentane and neopentane would appear to account for relatively lower heats of the latter hydrocarbon even with a molecularly rough surface. Of course the n-pentane molecules would be able to adapt their shape to a rough surface more readily than would those of neopentane.

Cyclopentane has been shown to consist essentially of rigid molecules in the form of puckered rings.[9] It seems reasonable that such rigid molecules would fit only imperfectly on an even slightly

rough surface, thus accounting for the low heats of adsorption compared to n-pentane. Presumably, however, the molecules of this hydrocarbon are capable of closer contact than are those of neopentane.

Although it is possible to relate the shape of the neopentane molecule to the low heat of adsorption of this hydrocarbon, it should be observed that the value of σ for neopentane reported in Table I appears to be anomalously high. Thus with only three $-CH_3$ groups in contact with the surface and one $-CH_3$ group definitely not in contact, we have a σ value of 57 sq. Å. compared to 45 for n-butane and 53 for n-pentane. We are unable to offer a very plausible explanation of this observation. Of course it is possible that the B. E. T. method does not give a true value of the volume of gas required to fill the monolayer in this case. A similar unexplained high value in σ has been reported in the case of krypton on several adsorbents.[10]

Summary

1. The isotherms and calorimetric heats of adsorption have been determined at 0° for n-butane, n-pentane, neopentane and cyclopentane on a sample of carbon black which has been extensively used for previous adsorption studies.

2. It is found that at 0.05 coverage of the surface, the contribution per $-CH_2$ group of the normal hydrocarbons is approximately 3 kcal. per mole.

3. It is found that the neopentane and the cyclopentane have heat values in which the contribution per $-CH_2$ or $-CH_3$ group is less than the 3 kcal. encountered with the normal hydrocarbons.

4. The explanation is suggested that the differences in the energies of binding of these pentanes as indicated from the heat measurements may be attributed to differences in geometric fit of their molecules to the carbon black surface.

(9) (a) Aston, Schuman, Fink and Doty, This Journal, **63**, 2029 (1941); (b) Spitzer and Pitzer, *ibid.*, **68**, 2537 (1946); (c) Spitzer and Huffman, *ibid.*, **69**, 211 (1947).

(10) Beebe, Beckwith and Honig, This Journal, **67**, 1554 (1945).

Catalysis of the Reaction of Carbon Monoxide with Iodine in Acid Solution[1]

By William Marshall MacNevin* and William Neuton Carson, Jr.[2,3]

The reaction between carbon monoxide and iodine in acid solution has not been reported in the literature. According to the free energy change, $\Delta F^0_{298.10} = -33,835$ cal./mole, the reaction should occur readily. Preliminary experiments indicated that it could be catalyzed appreciably.

A more extensive study of catalysts and conditions has therefore been made and is reported in this paper.

Preparation of Carbon Monoxide.—Carbon monoxide was prepared in an all glass apparatus by bubbling anhydrous formic acid into concentrated sulfuric acid at 100°. The gas was scrubbed with chloroform, 50% potassium hydroxide solution and alkaline pyrogallol. The apparatus was designed so the generator could be emptied of spent sulfuric acid and refilled without introducing air. The gas was stored over water.

Iodine Reaction.—The iodine reactor vessel consisted of a 200 mm. × 25 mm. Pyrex tube sealed at the lower end. Carbon monoxide was led through a 7-mm. tube sealed

into the base of the reactor tube. The upper end was fitted with the outer part of a 29/42 standard taper joint. The inner part of the upper joint was sealed and served as a cover for the reactor. A small condenser was sealed into the cap and served to condense iodine that might escape from the reactor. However, vaporization of iodine was not appreciable as shown by the low value of blank runs.

Carbon monoxide was passed into the reactor at a rate of 350 ± 25 ml. per minute maintained constant by means of a flow regulator.[4] The depth of iodine solution through which the carbon monoxide passed in the reactor was about 7 cm. The pressure of the carbon monoxide gas entering the reactor was approximately atmospheric.

Two platinum wires were sealed through the walls of the reactor and were used for the application of the dead-stop electrometric method of end-point detection of Foulk and Bawden.[5] The completion of the reaction with iodine was indicated by cessation of current resulting from polarization of an electrode. When the iodine had not completely reacted, the reactor tube was removed and the remaining iodine titrated with thiosulfate.

The temperature of the reactor was held thermostatically at 25 ± 0.01°. The reactor was protected from light in order to eliminate photochemical effects.

Measurement of Rate.—Measurements of rate were made by observing either how long a time was required for a fixed rate of flow of carbon monoxide to discharge a given amount of iodine or, if the rate was slow, by determining the amount of iodine reduced in one hour. The rate is expressed in moles of iodine per liter per minute.

Effect of Catalysts.—The effect of different catalysts on the reaction was determined by bubbling carbon monoxide at a constant rate through 36 ml. of solution consisting of 25 ml. of buffer solution, 10 ml. of 0.1 N iodine in 10% potassium iodide solution and 1 ml. of catalyst solution. Solutions (0.1 N) of cupric chloride, stannous chloride, ferrous chloride, nickel chloride, ammonium molybdate and ceric sulfate were tried as catalysts. Solutions (0.5%) of chloroauric acid, rhodium chloride, palladous chloride, chloroplatinic acid and osmium tetroxide were also used. In two experiments, the catalyst was 1 ml. of carbon tetrachloride and 1 ml. of chloroform respectively. Of these catalysts, only palladium and rhodium showed marked effects and it was therefore decided to select palladous chloride as the catalyst for all subsequent experiments.

Concentration of Catalyst and Influence of pH.—Experiments on the effect of variations in concentration of palladous chloride catalyst and variations in pH were combined. Three concentrations of palladous chloride, 0.01, 0.001 and 0.0001 M, were prepared in 0.1 M hydrochloric acid. In subsequent experiments, 1 ml. of catalyst solution was diluted to 36 ml.

Rates were determined in solutions of pH value 8.4, 6.4, 4.0, 0.2 and in 2, 3 and 4 M hydrochloric acid. Blank runs without any palladous chloride catalyst were made for each of the acidities. The data are summarized in Table I.

Discussion.—The data show that the rate of reaction is about constant for several pH units higher than pH 0.2. The rate is noticeably greater at higher concentration of palladous chloride. In alkaline solution the rate increases markedly. In very acid solutions the rate falls off sharply.

Palladous salts have long been noted for their catalytic effect on the oxidation of carbon monoxide by oxygen. Wieland[6] showed that oxidation by oxygen does not occur in the absence of water

(4) W. N. Carson, *Anal. Chem.*, **21**, 316 (1949)

(5) C. W. Foulk and A. T. Bawden, THIS JOURNAL, **48**, 2044 (1926).

(6) Heinrich Wieland, *Ber.*, **45**, 679–685 (1912).

TABLE I

EFFECT OF CONCENTRATION OF CATALYST AND pH ON RATE OF REACTION BETWEEN CARBON MONOXIDE AND IODINE

Expt.	pH	Concn. PdCl$_2$ molar $\times$ 36	I$_2$ initial[a] moles $\times 10^{+5}$	I$_2$ final[a] moles $\times 10^{+5}$	I$_2$ reacted[a] moles $\times 10^{+5}$	Time, minutes	Moles I$_2$ react. per l. per min. $\times 10^{+4}$
1	8.4	0.01	51.2	0	51.2	30	4.73
2	8.4	.001	51.2	0	51.2	44	3.23
3	8.4	.0001	51.2	14.8	36.4	60	1.68
4	8.4	0	51.2	32.4	18.8	60	0.87
5	6.4	0.01	51.2	0	51.2	31	4.60
6	6.4	.001	51.2	8.2	43.0	60	1.99
7	6.4	.0001	51.2	43.2	8.0	60	0.37
8	6.4	0	51.2	51.1	0.1	60	0.005
9	4.0	0.01	51.2	0	51.2	40	3.56
10	4.0	.001	51.2	8.2	43.0	60	1.99
11	4.0	.0001	51.2	46.0	5.2	60	0.24
12	4.0	0	51.2	50.8	0.4	60	0.02
13	0.2	0.01	53.7	0	53.7	40	3.72
14	0.2	.001	53.7	12.6	41.1	60	1.90
15	0.2	.0001	53.7	45.2	8.5	60	0.39
16	0.2	0	53.7	51.1	2.6	60	0.12
17	2 M HCl	0.01	55.0	0	55.0	40	3.82
18	2 M HCl	.001	55.0	24.1	30.9	60	1.43
19	2 M HCl	.0001	55.0	49.0	6.0	60	0.28
20	2 M HCl	0	55.0	52.2	2.8	60	0.13
21	3 M HCl	0.01	58.2	0	58.2	47	2.69
22	3 M HCl	.001	58.2	29.5	28.7	60	1.33
23	3 M HCl	.0001	58.2	48.5	9.7	60	0.45
24	3 M HCl	0	58.2	50.5	7.7	60	0.36
25	4 M HCl	0.01	56.0	11.1	44.9	60	2.08
26	4 M HCl	.001	56.0	38.5	17.5	60	0.81
27	4 M HCl	.0001	56.0	54.2	1.8	60	0.08
28	4 M HCl	0	56.0	55.2	0.8	60	0.04

[a] Also equal to the milliliters of 0.02 N thiosulfate required to titrate the iodine.

vapor. He states that the first product formed is formic acid, which is then split by the catalyst into carbon dioxide and hydrogen. The oxygen reacts with the hydrogen to regenerate water. In the course of the above experiments this theory was investigated. Carbon monoxide was bubbled through a solution of palladous chloride and palladium black quickly formed. The solution also acquired marked reducing power. The experiment was done in the following way. One ml. of 0.001 M palladous chloride in 0.1 N hydrochloric acid was diluted to 10 ml. with water. Carbon monoxide was bubbled through this solution at 25° at a rapid rate for one-half hour. At the end of this time 5.0 ml. of 0.01 N iodine was needed to give the starch end-point. Also, the palladium black formed during the initial reaction with carbon dioxide dissolved toward the end of the iodine titration. The presence of formic acid as suggested by Wieland was tested for by the method of Denigès[7] and none could be detected.

(7) G. Denigès, *Bull. soc. Phar. Bordeaux*, **51**, 151–154 (1911); *Pharm. J.*, **86**, 773 (1911).

This is a reducing power that can be due only to the reduced products formed by the reaction of carbon monoxide in the presence of palladous chloride and water. If iodine is present, palladium black does not form until the iodine is all consumed. This indicates that it is the palladium in solution which is the effective catalyst and not palladium black.

Additional evidence that palladium black is not the effective catalyst is shown by the reaction of vanadium solutions with carbon monoxide. Qualitative experiments were done using pervanadyl ion as the oxidizing agent. No formation of palladium black occurred as long as the yellow tint of the pervanadyl ion remained. When the reduction to vanadyl ion was complete, palladium black precipitated at once and no further reduction occurred. The absence of further reduction of vanadyl to vanadic ion also indicates the probable absence of adsorbed hydrogen on the surface of the palladium black. These experiments also indicate that the mechanism of the action of the palladium salt as a catalyst does not involve free hydrogen on the surface of palladium black.

Similar evidence that palladium black is not the effective catalyst is seen in the work of Shepherd[8] and co-workers who have used the catalytic effect of palladium in the detection and estimation of carbon monoxide in gases. Shepherd uses palladium sulfate to catalyze the formation of molybdenum blue by reduction of complex silicomolybdates

(8) Martin Shepherd, *Anal. Chem.*, 19, 77–81 (1947).

with carbon monoxide. The green to dark blue colors formed on the surface of the silica gel supporting the active reagents are clear, which indicates that the formation of palladium black cannot be appreciable.

This evidence supports the statements that dissolved palladium, probably palladous chloride, is the effective catalyst and that palladium black is not essential for the catalysis. Adsorbed hydrogen is therefore not involved in the reaction. The absence of hydrogen from the mechanism is also indicated by the fact that the rate over the pH range 0–ca. 6.4 is constant. While this evidence is not conclusive as to the over-all mechanism, it points to the probable existence of a two-valent palladium couple constantly undergoing reduction and oxidation.

Summary

1. The reaction $CO + I_2 + H_2O = CO_2 + 2HI$ in acid solution has been found to be strongly catalyzed by palladous chloride.

2. Measurements of relative rates of the reaction show the rate to be essentially constant over pH range 0 to ca. 6.

3. The absence of formic acid and of adsorbed or free hydrogen is indicated.

4. The palladium catalyst has been shown to be effective in the dissolved state and not as palladium black.

The Ultraviolet Absorption Spectra of Substituted Bitolyls

BY LUCY W. PICKETT,* MARIAN GROTH, SUSAN DUCKWORTH AND JANICE CUNLIFFE

The effect of steric hindrance on the ultraviolet absorption spectra of biphenyls has been studied by a number of investigators, some of whom are cited here.[1,2,3,4,5,6] It has been generally recognized that an increase in the intensity of absorption may be correlated with the approach to coplanarity of the benzene rings and hence to the extent that resonance structures involving both rings are possible. The present study of a group of bitolyls, namely, 6,6'-dinitro-2,2'-bitolyl, 5,5'-dinitro-2,2'-bitolyl, 6,6'-diamino-2,2'-bitolyl (I), 5,5'-diamino-2,2'-bitolyl (II), 4,4'-diamino-2,2'-bitolyl (III), 4,4'-diamino-3,3'-bitolyl (IV), as well as the hydrochlorides of the last four compounds is of interest in this connection. Kuhn

* Harvard University, Lalor Fellow, 1938.

(1) Pickett, Walter and France, THIS JOURNAL, 58, 2296 (1936).

(2) O'Shaughnessy and Rodebush, *ibid.*, 62, 2906 (1940).

(3) Williamson and Rodebush, *ibid.*, 63, 3018 (1941).

(4) Pestemer and Mayer-Pitsch, *Monatsh.*, 70, 104 (1937).

(5) Jones, THIS JOURNAL, 63, 1658 (1941).

(6) Sherwood and Calvin, *ibid.*, 64, 1350 (1942).

and Rometsch[7] have reported measurements of the absorption, rotation dispersion and circular dichroism of I. The absorption curves for 4,4'-dinitro-2,2'-bitolyl and 4,4'-dinitro-3,3'-bitolyl have been determined.[6]

Experimental

Preparation of Compounds.—These compounds have all been reported in the literature[8] so that details are given only where procedures differed from those published.

6,6'-Dinitro-2,2'-bitolyl.—This was prepared by Ullmann synthesis from 2-iodo-3-nitrotoluene and purified by repeated crystallization from absolute alcohol; m. p. 110.8–111.3° (cor.).

6,6'-Diamino-2,2'-bitolyl.—The compound just described was reduced by stannous chloride in glacial acetic acid.[9] By the following slightly modified procedure a better yield was obtained: 4 g. of the nitro compound was suspended in 12 ml. of glacial acetic acid and to this was added 40 g. of stannous chloride in 100 ml. of concentrated hydrochloric acid. The mixture was stirred for two hours,

(7) Kuhn and Rometsch, *Helv. Chim. Acta*, 27, 1080, 1346 (1944).

(8) Fanta, *Chem. Revs.*, 38, 139 (1946).

(9) Kenner and Stubbings, *J. Chem. Soc.*, 119, 600 (1921).