727. *Synthetical Applications of Activated Metal Catalysts. Part XV.*[1] *The Catalytic Toxicities of the Phenyl Derivatives of the Typical Elements of Groups V, VI, and VII, and their Hydrogenolysis by W-7 Raney Nickel.*

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Except for triphenylamine, diphenylamine, aniline, and diphenyl ether, the compounds implied in the title give benzene in yields exceeding 80% when treated with W-7 Raney nickel in methanol. Under these conditions diphenyl ether is converted into a mixture of benzene and cyclohexanol, and the amines are hydrogenated. These results have been correlated with the poisoning coefficients of these compounds. It is suggested that phenyl derivatives which are hydrogenolysed are adsorbed preferentially *via* their hetero-atoms, while the amines interact with the catalyst predominantly through their aromatic electrons.

During the past two decades Raney nickel catalysts have been used widely to bring about the hydrogenolysis of organic sulphur compounds. In discussing the mechanism of these

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[1] Part XIV, Badger, Cheuychit, and Sasse, *J.*, 1962, 3241.

reactions, Hauptmann and Wladislaw[2] suggested that hydrogenolysis of an organic molecule is preceded by its adsorption on the catalyst *via* the sulphur atom. This hypothesis, which has been widely accepted,[3] has not been proved, but it is compatible[4] with current views concerning the mechanism of the poisoning by sulphur compounds of metal catalysts in hydrogenations.[5]

The fact that organic derivatives of chlorine, bromine, and iodine, which are readily hydrogenolysed by Raney nickel,[6] also lower the activity of W-4 Raney nickel in the hydrogenation of styrene,[7] suggests that the preferential adsorption of organic halides on Raney nickel represents the first stage in their hydrogenolysis. Since derivatives of the higher analogues of sulphur and of the typical elements of Group V are known to poison platinum catalysts,[5] the question arises whether compounds of these elements can be adsorbed by Raney nickel also, and whether this may lead to their hydrogenolysis by this catalyst.

In the present paper we have studied this problem by examining the stability towards hydrogenolysis by W-7 Raney nickel of each of the phenyl derivatives of the (stable) typical elements of Groups V, VI, and VII. The results obtained have been correlated with a second series of experiments in which we have determined the effect of each of these compounds on the rate of hydrogenation of *trans*-crotonic acid in the presence of W-7 Raney nickel.

EXPERIMENTAL

Materials.—Methanol and *trans*-crotonic acid were purified as described earlier.[8] The following compounds were commercial samples which were purified by repeated crystallisation or fractional distillation: benzene, b. p. 80°, n_D^{25} 1·4980; fluorobenzene, b. p. 85°, n_D^{25} 1·4620; chlorobenzene, b. p. 131—132°, n_D^{25} 1·5214; bromobenzene, b. p. 155—156°, n_D^{21} 1·5592; iodobenzene, b. p. 188°, n_D^{21} 1·6190; aniline, b. p. 184—185°, n_D^{21} 1·5857; diphenylamine, m. p. 52·5—53°; triphenylamine, m. p. 126·5—127°; diphenyl ether, b. p. 251—252°, m. p. 28—28·5°; diphenyl sulphide, b. p. 155°/13 mm.; triphenylphosphine, m. p. 80·5—81°. The following compounds were prepared and purified by standard procedures in an atmosphere of nitrogen; diphenyl selenide,[9] b. p. 166—167°/12 mm.; diphenyl telluride,[10] b. p. 175—176°/12 mm., triphenylarsine,[11] m. p. 61—51·5°; triphenylstibine,[12] m. p. 54·5—55°; triphenylbismuthine,[13] m. p. 78·5°. W-7 Raney nickel catalyst[14] prepared from 1 : 1 aluminium–nickel alloy (B.D.H.) was used throughout.

Hydrogenolyses.—General procedure. A solution of the phenyl derivative (monophenyl derivatives, 0·10 mole; diphenyl derivatives, 0·064 mole; triphenyl derivatives, 0·038 mole) in the minimum volume of warm methanol was added to a suspension of W-7 Raney nickel in the same solvent (prepared from 125 g. of alloy and washed by decantation first with 8 × 200 c.c. of water, then with 8 × 200 c.c. of methanol). This mixture was made up to 250 c.c. with methanol and refluxed for 2 hr. During this time gas escaping from the condenser was passed through a trap cooled by solid carbon dioxide–acetone. After the catalyst had been filtered off and washed with hot methanol (4 × 50 c.c.), the filtrate and washings were combined with the condensate collected in the trap and fractionally distilled through a jacketed column (2 × 60 cm.) packed with single-turn glass helices. All material boiling below 64·5° (reflux ratio 1 : 12) was collected in one fraction, and a second fraction, b. p. 64·5° (50 c.c.), was taken.

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[2] Hauptmann and Wladislaw, *J. Amer. Chem. Soc.*, 1950, **72**, 710.

[3] Bonner, *J. Amer. Chem. Soc.*, 1952, **74**, 1034; Weitkamp, *ibid.*, 1959, **81**, 3434; Badger and Sasse, *J.*, 1957, 3862.

[4] Sasse, Ph.D. Thesis, Adelaide, 1956.

[5] Maxted, *Adv. Catalysis*, 1951, **3**, 129.

[6] Schwenk, Papa, and Ginsberg, *Ind. Eng. Chem., Analyt. Ed.*, 1943, **15**, 576.

[7] Pattison and Degering, *J. Amer. Chem. Soc.*, 1951, **73**, 611.

[8] Badger, Jackson, and Sasse, *J.*, 1960, 4438.

[9] Leicester, *Org. Synth.*, 1938, **18**, 27.

[10] Lederer, *Ber.*, 1911, **44**, 2287.

[11] Shriner and Wolf, *Org. Synth.*, 1950, **30**, 95.

[12] Hiers, *Org. Synth.*, Coll. Vol. I, 1932, 535.

[13] Pfeiffer, Heller, and Pietsch, *Ber.*, 1904, **37**, 4620; Classen and Ney, *Z. anorg. Chem.*, 1921, **115**, 253.

[14] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695.

Preliminary experiments had shown that these two fractions contained 95 ± 3% of the benzene present in four mixtures containing methanol, benzene (0·1—3 vol. %), and water (5 vol. %). The concentration of benzene in these fractions was determined by gas–liquid partition chromatography, with mixtures of benzene and methanol of known concentrations as standards. With each phenyl derivative the benzene formed in one experiment was isolated by gas–liquid partition chromatography and identified by its ultraviolet and infrared spectra. The average yield of benzene observed in at least two experiments with each phenyl derivative is recorded in Table 2. The residue left after distillation of the fractions containing benzene was diluted with water and extracted with ether. These extracts were examined for the presence of organic compounds as described below.

Triphenylamine. The ethereal extract of the residue of the distillation was extracted with 10% hydrochloric acid to separate a basic fraction (0·7 g.). This was recrystallised from ethanol to give colourless needles (0·3 g.) of tricyclohexylamine, m. p. 161—162° alone and mixed with an authentic sample.[15] From the non-basic fraction triphenylamine (8·5 g.), m. p. 162—163°, was isolated.

Diphenylamine. The residue from the distillation recrystallised from light petroleum, to give diphenylamine (3·8 g.), m. p. 52°. The liquors of this crystallisation were diluted with ether and shaken with 10% hydrochloric acid, which precipitated a colourless solid. This crystallised from aqueous hydrochloric acid to give colourless needles (0·5 g.) of dicyclohexylammonium chloride, m. p. 344—345°, alone and mixed with an authentic sample.[16] The non-basic filtrate gave diphenylamine (3·2 g.), m. p. 52—53°.

Aniline. Distillation of the filtrate gave the following fractions: (*a*) b. p. 55—64·5° (11 c.c.); (*b*) b. p. 64·5° (50 c.c.); (*c*) b. p. 64·5—65° (290 c.c.). Benzene was not detected in fractions (*b*) and (*c*) which were combined and acidified with hydrochloric acid. Evaporation gave a colourless solid (2·2 g.), m. p. 185—195°. Crystallisation from dilute hydrochloric acid gave needles of cyclohexylammonium chloride (2·0 g.), m. p. and mixed m. p. 203—204°. From the residue from the distillation aniline (6·8 g.), b. p. 183—184°, was isolated.

Diphenyl ether. The ethereal extract of the residue left after the removal of the fractions containing benzene was distilled, giving cyclohexanol (4·1 g.), b. p. 157—158°, n_D^{25} 1·4640. A second fraction (0·4 g.), b. p. 250—252°, was diphenyl ether. The aqueous phase left after extraction of the cyclohexanol and diphenyl ether was treated with an excess of bromine water, to give a pale yellow precipitate (0·4 g.). Crystallisation from ethanol gave colourless needles (0·3 g.), m. p. 95° alone and mixed with authentic 2,4,6-tribromophenol.

Hydrogenolysis of Triphenylphosphine, Triphenylarsine, Triphenylstibine, Triphenylbismuthine, Diphenyl Sulphide, Diphenyl Selenide, Diphenyl Telluride, Fluorobenzene, Chlorobenzene, Iodobenzene.—Each of these compounds gave, apart from benzene, less than 0·3 g. of ether-soluble organic matter. These products were not examined.

Benzene.—A solution of benzene (10 c.c.) in methanol was treated with the catalyst and worked up as described above. Two fractions were separated by distillation: (*a*) b. p. 53—64·5° (32 c.c.); (*b*) b. p. 64·5° (50 c.c.). The presence in fraction (*a*) of benzene (28 vol. %), methanol (68 vol. %), and cyclohexane (3 vol. %) was shown by gas–liquid partition chromatography. The cyclohexane was separated by gas–liquid partition chromatography and identified by its infrared spectrum. No benzene or cyclohexane could be detected in fraction (*b*) by gas–liquid partition chromatography.

Gas–Liquid Partition Chromatography.—Analyses of mixtures of benzene and methanol were carried out in a Griffin V.P.C. apparatus Mark II with a 6-ft. column packed with Celite [60—80 mesh; coated with 15% (wt.) of Apiezon L] at 110°. Preparative work was carried out with a Beckman Megachrom preparative gas-chromatograph, with eight 6-ft. columns packed with C-22 firebrick [42—60 mesh; coated with Apiezon J (35%)].

Hydrogenations.—The method used for the hydrogenations and for the evaluation of the results has been described before.[8] Because of the number of hydrogenations, runs were carried out simultaneously in two microhydrogenators at 30° ± 0·2°, and several preparations of the catalyst had to be used. The activities of these varied from 1·60—1·65 c.c./min. and, provided the catalysts were stored at 2°, no change in the activity of individual batches could be detected within 5 days. Before addition of crotonic acid (0·00012 mole), the catalyst (0·01—0·2 g.) was equilibrated with the poison (in most runs 0·000006 mole; exceptions are noted in Table 1)

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[15] Adkins, Zartman, and Cramer, *J. Amer. Chem. Soc.*, 1931, **53**, 1425.

[16] Hiers and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 1101.

for 65 min. (the rate of shaking of hydrogenation flasks throughout this work was 290 ± 20 vibrations per min.). After completion of a run, the catalyst was filtered off, washed, dried, and weighed. The results of individual experiments are given in Table 1; poisoning coefficients calculated according to Maxted's method are given in Table 2. Duplicate experiments showed that poisoning coefficients which are larger than about 5×10^2 are reproducible by the present

TABLE 1.

Hydrogenations of crotonic acid.

Wt. of catalyst (g.)	Initial rate (c.c./min.)	Poison	Wt. of catalyst (g.)	Initial rate (c.c./min.)	Poison	Wt. of catalyst (g.)	Initial rate (c.c./min.)	Poison
0·0638	2·10	—	0·0186	0·50	PPh_3	0·1000	0·78	Ph_2Se *
0·0463	1·52	—	0·0152	0·38	,,	0·1170	0·75	,,
0·0300	0·91	—	0·1003	2·26	$AsPh_3$	0·1070	0·82	,,
0·0250	0·76	—	0·0458	1·07	,,	0·1760	1·26	,,
0·0269	0·55	C_6H_6	0·0084	0·11	,,	0·1852	0·85	Ph_2Te *
0·0637	1·62	,,	0·0192	0·47	,,	0·1496	0·66	,,
0·0570	1·61	,,	0·0250	0·50	$SbPh_3$	0·0800	0·16	,,
0·1305	3·42	,,	0·0510	0·87	,,	0·1912	0·71	,,
0·2357	6·02	NH_2Ph	0·0082	0·11	,,	0·0916	3·39	—
0·0185	0·72	,,	0·0186	0·35	,,	0·0250	0·68	—
0·0543	0·32	,,	0·0622	0·90	$BiPh_3$	0·0250	0·90	—
0·0305	0·54	,,	0·0729	0·97	,,	0·0272	0·78	—
0·0150	0·49	—	0·0998	2·69	,,	0·0356	0·85	PhF
0·0134	0·36	—	0·0180	0·24	,,	0·0274	0·68	,,
0·0424	1·23	—	0·0186	0·42	—	0·0306	0·86	,,
0·0482	1·69	—	0·0202	0·68	—	0·0574	1·36	,,
0·0350	1·04	$NHPh_2$	0·0590	1·93	—	0·0658	0·80	PhCl
0·0372	1·51	,,	0·0698	2·08	—	0·0368	0·42	,,
0·0216	0·51	,,	0·0216	0·49	Ph_2O	0·0162	0·09	,,
0·0304	0·88	,,	0·0484	0·90	,,	0·0350	0·43	,,
0·0850	2·46	NPh_3	0·1292	2·70	,,	0·1068	0·84	PhBr
0·0298	0·78	,,	0·0704	1·50	,,	0·0776	0·58	,,
0·0100	0·27	,,	0·1940	1·93	Ph_2S *	0·0470	0·31	,,
0·0238	0·65	,,	0·2090	1·81	,,	0·0438	0·18	,,
0·0412	1·26	—	0·0494	0·39	,,	0·1128	0·54	PhI
0·0648	2·09	—	0·0414	0·27	,,	0·0882	0·43	,,
0·0300	1·13	—	0·0206	0·71	—	0·0300	0·09	,,
0·0112	0·22	—	0·0136	0·45	—	0·0592	0·16	,,
0·0238	0·57	PPh_3	0·1348	3·88	—			
0·0089	0·20	,,	0·0480	1·51	—			

* 0·000003 mole.

TABLE 2

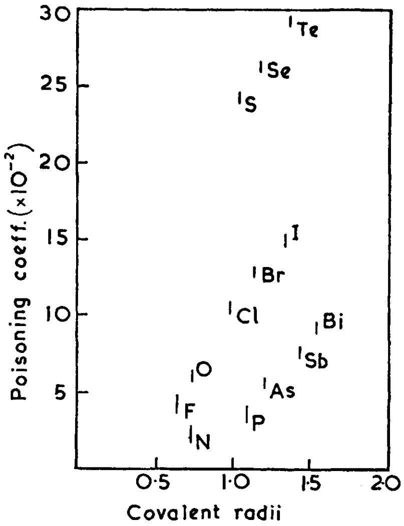
Compound	Yield of benzene %	Other products identified	Activity * (c.c./min.)	Poisoning coeff. ($\times 10^{-2}$) †
C_6H_6	—	Cyclohexane (10%)	1·32	3·1
NPh_3	0·25	Tricyclohexylamine (3%) ‡	1·41	2·2
$NHPh_2$	4	Dicyclohexylamine (4%)	1·41	2·2
NH_2Ph	0·25	Cyclohexylamine (16%)	1·13	2·5
PPh_3	90	—§	1·31	3·5
$AsPh_3$	87	—§	1·10	5·6
$SbPh_3$	89	—§	0·91	7·6
$BiPh_3$	85	—§	0·73	9·2
Ph_2O	35	Cyclohexanol (33%) Phenol (1·5%)	1·05	6·1
Ph_2S	92	—§	0·45	24·3
Ph_2Se	88	—§	0·36	26·3
Ph_2Te	85	—§	0·20	29·3
PhF	82	—§	1·24	4·2
PhCl	86	—§	0·67	10·6
PhBr	85	—§	0·36	13·0
PhI	88	—§	0·18	14·9

* Unpoisoned catalysts, 1·60—1·65 c.c./min. † The poisoning coefficients in Table 3, ref. 8, should be multiplied by 10^{-2}, *not* 10^{-4}. ‡ Approx. 4% of other basic products were not identified. § Less than 0·3 g. of ether-soluble organic matter was isolated but not identified.

method within 0·3 × 10^2. Poisoning coefficients between 1·5 × 10^2 and 5 × 10^2 can be reproduced within 0·5 × 10^2.

Results and Discussion

Hydrogenolysis.—All the phenyl derivatives examined gave benzene when exposed to an excess of W-7 Raney nickel in boiling methanol (Table 2). As expected, yields of benzene exceeding 80% were obtained from the derivatives of sulphur,[17] selenium,[18] chlorine, bromine, and iodine; [6,19] but it is noteworthy that the derivatives of phosphorus, arsenic, antimony, bismuth, tellurium, and fluorine were equally readily hydrogenolysed, whereas such reactions appear to have been observed previously with only one organic derivative each of phosphorus,[20] arsenic,[19] and fluorine.[21]



Relation of covalent radii and Periodic Group to poisoning coefficient for Raney nickel in hydrogenation of *trans*-crotonic acid.

In view of previous reports,[19,22] it was surprising that W-7 Raney nickel in boiling methanol converted diphenyl ether in 70% yield into a mixture of benzene and cyclohexanol. A trace of phenol was also formed. Triphenylamine was largely recovered, and only traces of benzene and tricyclohexylamine could be isolated. Since the electronic and steric effects of the phenyl groups in triphenylamine should reduce the availability of the nitrogen atom for adsorption on the catalyst, aniline and diphenylamine were also examined. These bases underwent hydrogenation more readily to give cyclohexylamines, but still yielded only traces of benzene.

Under the conditions used in the present work, benzene gave cyclohexane in 10% yield.

Catalytic Toxicities.—All the phenyl derivatives examined lower the activity of W-7 Raney nickel in the hydrogenation of *trans*-crotonic acid, but the poisoning coefficients of individual compounds varied widely (Table 2). However, within each Group the poisoning coefficients increase with the size of the hetero-atom. Moreover, within the accuracy of the present method and with the exception of the derivatives of nitrogen and oxygen, the relationship in each Group between the poisoning coefficients and the covalent radii [23] of the hetero-atoms is approximately linear (cf. Figure).

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[17] Mozingo, Wolf, Harris, and Folkers, *J. Amer. Chem. Soc.*, 1943, **65**, 1013.

[18] Wiseman and Gould, *J. Amer. Chem. Soc.*, 1954, **76**, 1706; Hauptmann and Walter, *ibid.*, 1955, **77**, 4929.

[19] Schwenk, Papa, Whitman, and Ginsberg, *J. Org. Chem.*, 1944, **9**, 1.

[20] Doak and Freedman, *J. Amer. Chem. Soc.*, 1953, **75**, 6307.

[21] Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.

[22] Komatsu and Masumoto, *Bull. Chem. Soc. Japan*, 1931, **5**, 241.

[23] Pauling, " Nature of the Chemical Bond," 3rd edn., Cornell Univ. Press, 1960.

In each Period, the largest poisoning coefficient is associated with the derivative of the element of Group VI, and the smallest poisoning coefficient is observed with the derivative of Group V. Since these coefficients are determined after equilibration of the poison with the catalyst, this trend may be related in the higher Periods to the relative rates of hydrogenolysis of these compounds, as at room temperature in 0·001M-solution the rates of hydrogenolysis increase in the order diphenyl sulphide, chlorobenzene, triphenylphosphine.[24]

Since benzene poisons W-7 Raney nickel (Table 2), it may be expected that phenyl derivatives can interact with the catalyst, not only through their hetero-atoms, but also through their aromatic electrons. Table 2 shows also that the phenyl derivatives whose poisoning coefficients exceed that of benzene are hydrogenolysed, while the amines, which are less poisonous, are mainly hydrogenated. This finding is consistent with the hypothesis that the amines—like benzene—interact with W-7 Raney nickel preferentially through their aromatic electrons and that adsorption of these compounds *via* their nitrogen atoms is of minor importance. This view is supported by the fact that the three amines examined have almost identical poisoning coefficients. Moreover, the Figure shows that the mode of adsorption of triphenylamine differs from the way in which the triphenyl derivatives of the higher elements of Group V are adsorbed by W-7 Raney nickel. We suggest that these compounds as well as the derivatives of Groups VI and VII are chemisorbed predominantly *via* their hetero-atoms, and we propose that this mode of adsorption is a prerequisite for the occurrence of hydrogenolysis. The Figure indicates also that the poisoning coefficient of diphenyl ether lies in the range of the halogenated benzenes, suggesting that the species responsible for the poisoning may be the phenoxide ion; this hypothesis is being examined.

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[24] Sasse, unpublished work.