frequent handling of the solution some loss in hydrogen chloride was involved, but it is believed that this loss was negligible.

Conclusion

The curves showing the specific rotation for celluloses from spruce, yellow birch, Douglas fir, and cotton in solution in concd. hydrochloric acid, exhibit marked differences, indicating a difference in either the primary or the secondary reactions, which in turn would point to a difference in the celluloses themselves.

A marked similarity was observed between the curves for cotton and white spruce celluloses. It is known that cotton hydrolyzes only to glucose, while a large percentage of the sugar formed by the hydrolysis of white spruce is mannose, which has a much smaller specific rotation than glucose, so that the solution of hydrolyzed white spruce should show a lower specific rotation than that of cotton cellulose. The curves for cellulose from Douglas fir and yellow birch are also similar in character, although the former contains 5.5% of pentosan while the latter contains as high as 28% of pentosan. This great variation in composition should cause a distinct difference in the specific rotations, but such is not the case, as may readily be seen from the curves.

In view of these facts we are forced to admit with Cunningham[10] that the optical method for determining the quantitative conversion of cellulose to sugar is of little value. It does, however, indicate that considerable differences exist between celluloses from different sources; otherwise, all the curves would be identical in shape.

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THE ISOSTERISM OF PHENYL ISOCYANATE AND DIAZOBENZENE-IMIDE

BY WALLACE H. CAROTHERS

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It was the purpose of the investigation the results of which are reported in this paper to test experimentally a prediction arising from the octet theory of the structure of atoms and molecules.

The structural formula of phenyl isocyanate is usually represented as $C_6H_5—N=C=O$ (1), and of diazobenzene-imide as $C_6H_5—N=N\equiv N$ (2), or as $C_6H_5—N\langle{}^{N}_{N}\rangle$ (3). Applying the principles of the theory of atomic structure originated by G. N. Lewis[1] these would be $C_6H_5:\ddot{N}::C::\ddot{O}:$

[10] Cunningham, *Trans. Chem. Soc.*, **113**, 173 (1918).

[1] Lewis, THIS JOURNAL, **38**, 762 (1916).

(1A), $C_6H_5:\ddot{N}::N::\ddot{N}:$ (2A), and $C_6H_5:\ddot{N}\genfrac{}{}{0pt}{}{\ddot{N}}{\underset{\cdot\cdot}{N}}::$ (3A).[2] If it is assumed that the azo-imide has the structure 2A and the isocyanate the structure 1A then these 2 molecules have the same number of extra nuclear electrons arranged in the same way and differ only in the magnitude of the nuclear charges of some of the atoms. They should, therefore, be very similar in their physical properties. Langmuir[3] who pointed out this implication of the

[2] Since the validity of one of the conclusions of this paper depends upon the justness of the assumption that no other structures than 1A, 2A and 3A are probable for these 2 substances, it may be well to present some arguments in defense of this assumption. The valences here concerned are typically non-polar so that 1A, 2A and 3A may be represented as R—N=C=O (1B), R—N=N=N (2B) and R—N$<\genfrac{}{}{0pt}{}{N}{N}\|$ (3B), and these formulas will have the same significance as ordinary structural formulas with the added significance that each bond represents a pair of electrons shared between 2 atoms. Other formulas are possible, such as R—N≡N—N, R—N$<\genfrac{}{}{0pt}{}{N}{N}|$, R—N—N≡N for the azo-imide, and R—N≡C—O, R—N$<\genfrac{}{}{0pt}{}{C}{O}|$, R—C—N≡O, R—O=C=N, etc., for the isocyanate. To decide among the possibilities, the chemical evidence is examined, and leads to Formulas 1, 2, and 3, of which 1 and 3 may be represented by identical formulas 1B and 3B in terms of the octet theory, and the second by R—N=N=N (2B).

The question now is whether any of these possible structures other than 1B, 2B and 3B is consistent with the chemical evidence.

It might be thought that the familiar reactions of the isocyanates with R′OH, $R'NH_2$, etc., could be represented by R—N≡C—O. This is true. But the acceptance of this formula involves one of two assumptions: (a) the urethans and ureas have the formulas R—NH=C(—O)—OR′ and R—NH=C(—O)—NHR′ instead of the structures usually assigned to them, or (b) rearrangement of bonds takes place after the reaction. The usual formula, R—N=C=O, obviously has the advantage of simplicity and naturalness. Moreover, the formula R—N≡C—O is inherently improbable on the basis of the octet theory itself. It represents the nitrogen atom as having completed its sheath by sharing more than 3 pairs of electrons and the oxygen atom as having completed its sheath by sharing only 1 pair of electrons; in the absence of any definite force necessitating such arrangement the substance should spontaneously rearrange into R—N=C=O in accordance with the principle that the "charge" on each atom tends toward a minimum [See Langmuir, *Science*, **54**, 59 (1921)].

The corresponding formula, R—N≡N—N, for the azo-imide is still less satisfactory. It conflicts still more violently with the principle above mentioned, and for the same reason would spontaneously rearrange into R—N=N=N. Moreover, it scarcely represents any of the chemical properties of the azoimide. Thus, RN_3 reacts with R′MgBr to form R—N=N—NHR′ {*Ber.*, **38**, 670 (1905); **39**, 3905 (1906)}, whereas the structure R—N≡N—N requires that the R′ be attached to the first or second nitrogen atom.

Of the other formulas for R—N_3 and RNCO possible on the basis of the octet theory, many are obviously entirely incompatible with the chemical evidence and all are less probable than those which have been considered in drawing the conclusions here presented.

[3] Langmuir, THIS JOURNAL, **41**, 1543 (1919).

octet theory gave the name isosterism to this type of relationship between molecules. He presented evidence of the existence of isosterism between some pairs of gases and between numerous pairs of crystalline solids. Lack of sufficient data prevented complete verification of his prediction[3] that cyanic and hydrazoic acids are isosteric; and no data have been presented on liquid isosteres. The lack of data on cyanic and hydrazoic acids is probably due to their instability. Some of the organic isocyanates and azoimides, which may be regarded as derived from these acids are, however, much more stable; and as the phenyl derivatives are easily available and liquid at ordinary temperatures, it was thought worth while to study some physical properties of these derivatives.

The densities, vapor pressures and viscosities were measured at various temperatures and the following values obtained.

TABLE I

DENSITIES, VAPOR PRESSURES AND VISCOSITIES OF PHENYL ISOCYANATE AND PHENYL AZO-IMIDE

Absolute Densities			Vapor Pressure in mm. of Hg.		
Temperature °C.	PhNCO	PhN_3	Temperature °C.	PhNCO	PhN_3
0.0	1.1152	1.1175	75.0	36.3	33.8
10.0	1.1049	1.1070	80.0	45.3	41.8
20.0	1.0943	1.0968	85.0	55.9	52.0
30.0	1.0840	1.0864	90.0	68.2	63.6
40.0	1.0736	1.0762	95.0	83.9	79.1
50.0	1.0630	1.0657	..	...	...
Viscosities in Centipoises			Viscosities in Centipoises		
0.0	1.326	1.479	25.0	0.899	0.956
11.0	1.111	1.205	30.0	0.834	0.887
16.0	1.024	1.106	35.0	0.779	0.827
20.0	0.963	1.033	40.0	0.739	0.775

When these properties are plotted against the temperatures, smooth graphs are obtained and in each case the two curves are almost exactly parallel. The data may be summarized by means of conventional algebraic equations; t is the temperature.

Densities

Phenyl isocyanate $d = -0.001044t + 1.1152$

Diazobenzene-imide $d = -0.001044t' + 1.1152$, where $t' = t - 2.44°$.

Vapor Pressures

Phenyl isocyanate $p = 157 - 4.76t + 0.042t^2$

Diazobenzene-imide $p = 157 - 4.76t' + 0.042t'^2$, where $t' = t - 1.7°$

Viscosities

Phenyl isocyanate $\eta = 1.326 - 0.02163t + 0.000174t^2$

Diazobenzene-imide $\eta = 1.326 - 0.02163t' + 0.000174t'^2$, where $t' = t - 4.8°$.

The agreement between the values calculated by these formulas and the experimental ones is in each case practically within the limits of experi-

mental error, which for the densities is about ± 0.03%, and for the viscosities and vapor pressures about ± 0.7%.[4]

The properties of the isocyanate at any given temperature are thus the same as those of the azo-imide at temperatures from 1.7° to 4.8° higher, which is in accordance with the prediction. It is interesting to note also that the disparity between the properties of the two compounds is the same in type and degree as in the properties of the gaseous isosteres which Langmuir originally used to verify the principle of isosterism. The data here presented, then, confirm this principle. Incidentally they also confirm the straight-chain structure for triazo compounds, except that these should probably be written as R—N=N=N as Langmuir predicted[5] instead of as R—N=N≡N.[6]

Experimental Part

Diazobenzene-imide was prepared by the method of Fischer[7] as modified by Dimroth.[8] It was washed with dil. hydrochloric acid and sodium hydroxide several times, then with water, dried with calcium chloride, distilled under diminished pressure, treated with sodium and fractionated under diminished pressure into a Brühl receiver desiccated with phosphorus pentoxide. The phenyl isocyanate was a commercial sample prepared, presumably, from phosgene and aniline. It was treated with sodium and fractionated in the same way. Thus purified, it was water-white and developed no precipitate or turbidity after a month, even when occasionally exposed to the air.

Densities were determined by means of a pycnometer. Vapor pressures were determined by means of the static isoteniscope of Smith and Menzies.[9] The manometer was a simple U-tube 1 meter long and about 8 mm. in internal diameter fastened to a meter stick and made vertical. Readings were made with the naked eye by means of a mirror. The viscosities were determined with a Washburn viscosimeter[10] made from ordinary glass. Times of flow were determined simultaneously by means of 2 stop-watches, from 4 to 8 readings being made at each temperature.[11] All the data represent the means of various determinations, at least 2 different, freshly purified samples being used in each case. The temperatures were regulated by hand to about 0.05° during

[4] The calculated value for the viscosity of the azo-imide at 0° differs from the experimental value by about 3.6%, but since this calculation is equivalent to an extrapolation of the isocyanate curve into a region where the viscosity is changing very rapidly, the disagreement can hardly be considered as serious.

[5] Langmuir, THIS JOURNAL, **42**, 285 (1920).

[6] The structure R—N=N≡N is, of course, impossible from the point of view of the octet theory. The straight-chain structure for triazo compounds has been proposed and supported by Turrentine [THIS JOURNAL, **34**, 385 (1912); **36**, 23 (1914)], by Thiele [(*Ber.*, **44**, 2522 (1911)] and by Franklin [*Proc. 8th Inter. Cong. App. Chem.*, **6**, 119 (1912)] and the ring structure has been defended by M. O. Forster [*ibid.*, **6**, 108 (1912)].

[7] Fischer, *Ann.*, **190**, 92 (1878).

[8] Dimroth, *Ber.*, **35**, 1032 (1902).

[9] Smith and Menzies, THIS JOURNAL, **32**, 1412 (1910).

[10] Washburn, *ibid.*, **35**, 737 (1913).

[11] The viscometer was made of glass, and the water constant was determined at each temperature at which readings were made. In calculating the viscosities in centipoises from these readings the table of Bingham and Jackson [*Bur. Standards Sci. Papers*, **298**, p. 75] of the viscosity of water was used.

the measurements of densities and vapor pressures, and automatically to 0.005° or better in the determination of the viscosities.

Summary

Assuming the atoms of phenyl isocyanate and of diazobenzene-imide to be arranged as indicated in the formulas, C_6H_5NCO and C_6H_5NNN, application of the octet theory leads to the conclusion that they are isosteric. They should, therefore, be very similar in their physical properties. Their densities, vapor pressures and viscosities have been measured at various temperatures, and this prediction confirmed. These results also confirm the straight-chain structure for triazo compounds.

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DIACYL DERIVATIVES OF ORTHO-HYDROXYBENZYLAMINE

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Previous work in this Laboratory has shown (a) that when 2-acetyl-aminophenol is subjected to the action of benzoyl chloride (Schotten-Baumann reaction), the benzoyl radical is attached to nitrogen while acetyl migrates of oxygen;[1] (b) that this migration is not prevented by the presence of acid-forming substituents (halogen) attached to the nucleus of the aminophenol;[2] (c) that the acetyl-benzoyl derivatives of *p*-aminophenols do not suffer this rearrangement;[3] (d) that the presence of bromine and other heavy radicals adjacent to the reacting groups (amino and hydroxyl), which in many reactions causes marked retardation, does not prevent the migration;[4] and (e) that these observations seem to hold with bases derived from naphthalene, namely, 1-amino-2-naphthol and halogenated derivatives.[5] Since the acetyl-benzoyl derivatives of more than 15 *o*-amino-phenols, having various substituents at different positions in the molecule, have been tested in this way and all have been found to undergo this migration, it may be assumed that this behavior is general for this class of compounds when the acyl radicals are those specified.

Although the migration of this kind has thus far been observed to take place only in the derivatives of compounds in which both reacting groups

[1] Raiford, THIS JOURNAL, **41**, 2068 (1919).
[2] Raiford and Couture, *ibid.*, **44**, 1793 (1922).
[3] Raiford and Iddles, *ibid.*, **45**, 469 (1923).
[4] Woolfolk, unpublished report.
[5] Armstrong, unpublished report.