When we combine the value of ΔS^0 obtained from equation 15 with our value[6] for the entropy of LiOH (10.23 ± 0.05 e.u.) and with that of Latimer, Pitzer and Smith[27] for the entropy of the hydroxyl ion (−2.49 ± 0.06 e.u.) the standard state entropy of the lithium ion is

$$S^0_{25}\,(\mathrm{Li}^+) = 2.46 \pm 0.34 \text{ e.u.} \qquad (16)$$

This result compares with that, 4.7 ± 1.0 e.u., obtained by Brown and Latimer[28] from measurements of Li_2CO_3. Most of the discrepancy may have been due to Brown and Latimer being forced to use the heat of dilution of Li_2SO_4, in their computations, rather than that of Li_2CO_3, which was not available.

We can compute the heat and free energy of formation of the lithium ion in its standard state by combining the ΔH values of reactions 10 and 15 with those of the heat of formation of water[10] and the heat of ionization of water,[29] in conjunction with the standard entropies of Li,[18] Li^+ and H_2.[20] The following results are obtained

$$\text{Li(crystalline)} + \text{H}^+\text{(aqueous)} = \text{Li}^+\text{(aqueous)} + {}^1/_2\text{H}_2\text{(gas)} \qquad (17)$$

$$\Delta H^0_{25} = -66{,}706 \pm 100 \text{ cal.}$$

$$\Delta S^0_{25} = 11.37 \pm 0.40 \text{ e.u.}$$

$$\Delta F^0_{25} = -70{,}096 \pm 220 \text{ cal.}$$

In the above computations, the heat and free energy of formation of the hydrogen ion in its standard state are taken as zero, in accordance with the usual convention.

Finally, we can compute the standard oxidation potential of lithium from its standard free energy of formation. This computation yields

$$E^0 = 3.0383 \pm 0.0010 \text{ int. volts}$$

Summary

The heat capacity of Li_2O has been measured over the temperature range 16 to 304°K. Graphical integration of the heat capacity curve yields 9.06 ± 0.03 cal./mole/deg. for the entropy at 25°. When the entropies of LiOH and of steam are also considered, the curve yields a $\Delta S°$ of 33.70 ± 0.12 e.u. for the dissociation reaction $2LiOH = Li_2O + H_2O$(gas). This latter value is in good agreement with the value, 33.85, obtained from the dissociation equilibrium and confirms the application of the third law of thermodynamics to Li_2O.

A table of thermodynamic functions for Li_2O has been prepared for smoothed values of temperature.

Heats and free energies of formation have been computed for LiOH, $LiOH·H_2O$ and Li_2O, by combining their entropies with heat of solution and vapor pressure data.

The standard state entropy of the lithium ion at 25°, has been calculated as 2.46 ± 0.34 e.u. and the standard electrode potential of lithium as 3.0383 ± 0.0010 int. volts.

COLUMBUS 10, OHIO RECEIVED JULY 5, 1950

---

[27] W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

[28] O. L. I. Brown and W. M. Latimer, *ibid.*, **58**, 2228 (1936).

[29] K. S. Pitzer, *ibid.*, **59**, 2365 (1937).

[CONTRIBUTION NO. 1409 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

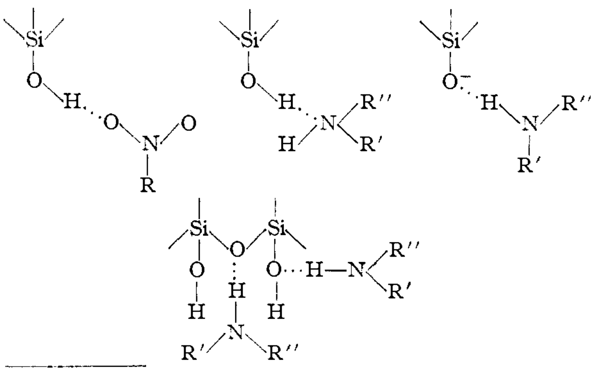
Hydrogen Bonding and Relative Adsorption Affinities on Silicic Acid of Certain Derivatives of Diphenylamine and N-Ethylaniline[1]

BY W. A. SCHROEDER

Introduction

The chromatographic investigations[2,3,4] of the products which are formed from diphenylamine and centralite (1,3-diethyl-1,3-diphenylurea) during their action as stabilizers of double base smokeless powder have resulted in the assembling of a detailed body of information on the chromatographic behavior on silicic acid of their nitro and nitroso derivatives and of those of N-ethylaniline. Consideration of the relative adsorption affinities of these compounds showed, however, that there was little evident regularity of behavior and that, for example, increase in the number of substituent or potential "anchoring" groups[5] was not necessarily accompanied by an increase in adsorption affinity as is so often the case, for instance, in the chromatography of the carotenoids.[6]

If one considers the structure of silicic acid, hydrogen bonding between it and amino and nitro compounds might be expected to take place in many ways such as



---

[1] Presented before the symposium on "The Specificity of Adsorbents," Division of Colloid Chemistry, Houston Meeting of American Chemical Society, March 28, 1950.

[2] W. A. Schroeder, *Ann. N. Y. Acad. Sci.*, **49**, 204 (1948).

[3] W. A. Schroeder, E. W. Malmberg, L. L. Fong, K. N. Trueblood, J. D. Landerl and E. Hoerger, *Ind. Eng. Chem.*, **41**, 2818 (1949).

[4] W. A. Schroeder, M. K. Wilson, C. Green, P. E. Wilcox, R. S. Mills and K. N. Trueblood, *ibid.*, **42**, 539 (1950).

[5] L. Zechmeister, *Am. Scientist*, **36**, 505 (1948).

[6] L. Zechmeister and L. Cholnoky, "Principles and Practice of Chromatography," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 26.

TABLE I

RELATIVE ADSORPTION AFFINITIES OF DERIVATIVES OF DIPHENYLAMINE ON SILICIC ACID–CELITE

4-Nitrosodiphenylamine[a] (XVIII)—most strongly adsorbed
Hexanitrodiphenylamine (XVII)
Pentanitrodiphenylamine (XVI)
4,4′-Dinitrodiphenylamine[b] (XV)
2,2′,4,4′-Tetranitrodiphenylamine (XIV)
2,4,4′-Trinitrodiphenylamine (XIII)
2,2′,4-Trinitrodiphenylamine (XII)
N-Nitroso-2,4′-dinitrodiphenylamine (XI)
4-Nitrodiphenylamine (X)
N-Nitroso-4,4′-dinitrodiphenylamine (IX)
2,4′-Dinitrodiphenylamine (VIII)
N-Nitroso-2-nitrodiphenylamine (VII)
2,4-Dinitrodiphenylamine (VI)
2,2′-Dinitrodiphenylamine (V)
N-Nitroso-4-nitrodiphenylamine (IV)
N-Nitrosodiphenylamine (III)
2-Nitrodiphenylamine (II)
Diphenylamine (I)———least strongly adsorbed

[a] The top three compounds were developed with mixtures of acetone in ligroin, the others with decreasing ratios of benzene in ligroin. [b] Position is uncertain; perhaps it should be higher.

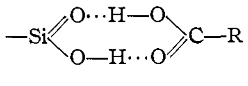
TABLE II

SUMMARY OF OBSERVED EFFECTS ON ADSORPTION AFFINITY CAUSED BY SUBSTITUTION OF GROUPS IN VARIOUS ENVIRONMENTS

Condition No.	Substitution of	Other substituents present	Effect of substn. on affinity	Comparison of effect with that under related conditions	Examples
1	4-Nitro	>NH (and 4-nitro)[a] but not 2-nitro groups	Increase	1 > 2 or 3 or 4 1 ≫ 5	I → X → XV I → X with I → II
2	4-Nitro into substituted ring	>NH and 2-nitro group(s)[a]	Increase	2 < 3 < 1	II → VI; V → XII
3	4-Nitro into unsubstituted ring	Same as 2	Increase	3 > 2 < 1	II → VIII; VI → XIII
4	4-Nitro	N-Nitroso (and 2- or 4-nitro)[a]	Increase	4 < 8; 4 < 1	III → IV → IX; VII → XI
5	2-Nitro	>NH (and 2-nitro)[a] but not 4-nitro groups	Increase	1st 2-nitro < 2nd 2-nitro; 2nd 2-nitro <2 or 3; 5 ≪ 1	I → II → V II → V with II → VI or VIII
6	2-Nitro	>NH and 4-nitro groups	Decrease	Comp. with 2 and 3	X → VIII; XV → XIII
7	2-Nitro	>NH, 2- and 4-nitro groups	Increase	7 < 2 or 3	VI or VIII → XII with V → XII
8	2-Nitro	N-Nitroso (and 4-nitro)[a]	Increase	8 > 4	III → VII; IV → XI
9	N-Nitroso	4-Nitro group(s)[a]	Decrease	Compare 9 and 10 with 4 and 8	X → IV; XV → IX
10	N-Nitroso	2-Nitro (and 4-nitro)[a] group	Increase		II → VII; VIII → XI

[a] The presence of groups given in parentheses does not alter the observed effect.

Indeed, Elder and Springer[7] have explained certain phases of the adsorption of fatty acids on silica gel by postulating the occurrence of bonds of the type



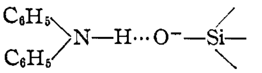
In the present article it has been possible to correlate qualitatively the relative adsorption affinities of certain derivatives of diphenylamine and N-ethylaniline with the strength of the hydrogen bonds which can be formed, by assuming that adsorption on silicic acid takes place primarily through hydrogen bonding.

Relative Adsorption Affinities of Diphenylamine and Derivatives.—Table I presents the relative adsorption affinities of some derivatives of diphenylamine in the order of increasing affinity from bottom to top when mixtures of benzene and ligroin are used as developers.

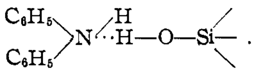
Examination of the data shows that not the number of substituent groups but rather the position of the group and the presence of other groups are the important factors in determining the adsorption affinity, as compounds II and X as well as other examples demonstrate. In order, then, to explain the observed adsorption sequence, it is necessary to decide how the position of the substituent group and the influence of other groups determine the ability of the molecule to form hydrogen bonds to the silicic acid. By a detailed consideration of the data, it was found that the introduction of a given group into a given type of environment results in each instance in a similar change in the affinity of the daughter compound relative to the parent. This information is summarized in Table II and will form the basis for discussion.

Discussion

Mode of Hydrogen Bonding of Anchoring Groups.—The "anchoring" groups which are responsible for the adsorption of these compounds are the amino, nitroso and nitro groups. Diphenylamine itself is weakly adsorbed because the amino group, its only anchoring group, is essentially neutral as evidenced by its ability to form either the potassium salt or the hydrochloride under anhydrous conditions. Accordingly, it has little tendency to form such hydrogen bonds as



or



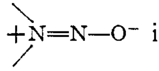
.

On the other hand, the presence of a nitroso or a nitro group in the molecule would be expected *per se* to lead to increased affinity relative to diphenylamine because both groups have abundant electron pairs with which to form hydrogen bonds with the silicic acid. The strength of such bonds

---

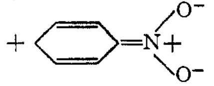
(7) A. L. Elder and R. A. Springer, *J. Phys. Chem.*, **44**, 943 (1940).

would be augmented by resonance forms of the type



$+\!>\!N=N-O^-$

in the nitroso group and of the type



in the nitro group: it is known that the strength of a hydrogen bond A–H···B is greater the more negative is the charge on B. Accordingly, the ability of other groups to affect the resonance of these groups should be a factor in determining the strength of the hydrogen bond and hence the position in the adsorption sequence.

Introduction of 2-Nitro and 4-Nitro Groups in the Absence of Each Other (Conditions No. 1 and 5).—The usually greater effect of a 4-nitro group as compared to a 2-nitro group is nowhere better illustrated than in 2-nitrodiphenylamine (II) and 4-nitrodiphenylamine (X). II is more strongly adsorbed than diphenylamine but so little more that the two cannot be separated into discrete zones with this type of developer whereas X is a rather strongly adsorbed substance. The unusually small increase in adsorption from I→II may be attributed to the formation of an intramolecular hydrogen bond in II as shown in Fig. 1.

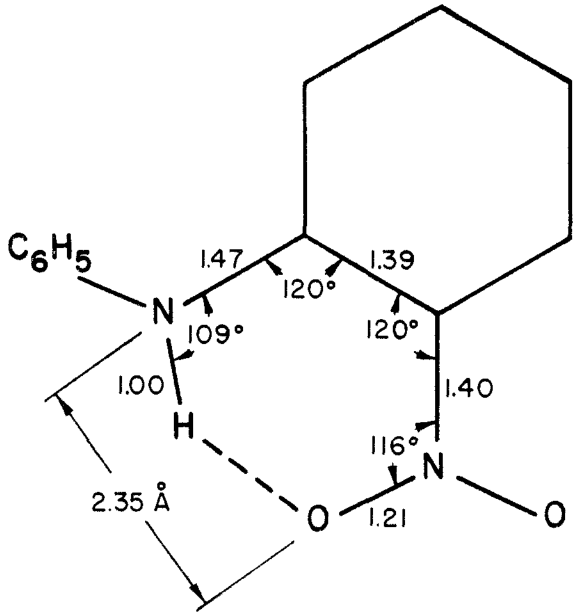
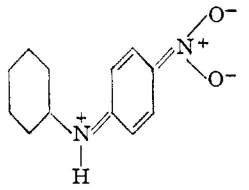


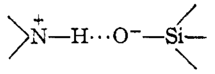
Fig. 1.—Atomic arrangement in 2-nitrodiphenylamine. Interatomic distances and bond angles have been given reasonable values.

The distance (2.35 Å.) which separates the amino nitrogen from the nitro oxygen atom is roughly 0.5 Å. shorter than the usual intermolecular hydrogen bond between nitrogen and oxygen atoms although a linear bond between the two may not be formed. This internal compensation of the hydrogen bonding ability of the 2-nitro group negates essentially the hydrogen bonding to the adsorbent so that II is only slightly more strongly adsorbed than I. This intramolecular hydrogen bonding also plays an important role in determining the adsorption affinity of the other derivatives.[7a] On the other hand, in X the nitro group is free to bond to the adsorbent. Indeed, the difference in adsorption from I→X is greater than when a nitro group is substituted under any other condition and will be discussed in the following section.

4-Nitro Substitution Under Several Conditions (Conditions No. 1 to 4).—Although 4-nitro substitution into any compound results in augmented affinity, the extent of the increase varies. The increase from I→X clearly is greater than II→VI or VIII and III→IV. In X, the presence of the nitro and amino group should result in good resonance with forms such as



and it may even be that the strong affinity of X is caused by hydrogen bonding of the amino group to the silicic acid. It has been found that in bonds of the type



$>\overset{+}{N}-H\cdots O^- -Si\!<$

the presence of a positive charge on the nitrogen atom significantly enhances the strength of the bond.[8] The presence of the intramolecular hydrogen bond or the N-nitroso group in IV, VI and VIII precludes any such conditions and these compounds accordingly have less affinity than X.

Some evidence of the importance of the >N–H group in X may be derived from the fact that 4-nitroaniline, 4-nitro-N-ethylaniline and 4-nitro-N,N-diethylaniline are adsorbed in this order of decreasing affinity from several solvents whereas, if hydrogen bonding to the nitro group determines the strength of adsorption, one might expect the last named to be the most strongly adsorbed for the following reason. The dipole moment of 4-nitro-N,N-dimethylaniline and presumably also that of the diethyl compound is greater than that of 4-nitroaniline.[9] Therefore, the charge separation is greater, the oxygens of the nitro group of 4-nitro-N,N-diethylaniline should be more negative, and it should be the most strongly adsorbed of the three whereas actually it is least strongly adsorbed.

Although compounds VI and VIII differ only in that in VI the 4-nitro group is in the same ring as the 2-nitro group whereas in VIII it is in the other ring, these derivatives are readily separable on silicic acid. The 4-nitro group in both probably determines the strength of adsorption largely

---

[7a] Note Added in Proof. Since this paper was submitted, H. Hoyer (*Kolloid-Z.*, **116**, 121 (1950)) has published an explanation of the relative adsorption affinities of hydroxyanthraquinones on silica gel on the basis of their ability or inability to form intramolecular hydrogen bonds. In agreement with the suggestion of the present paper that intramolecular hydrogen bonding in diphenylamine derivatives is responsible for decreased affinity, he finds that those hydroxyanthraquinones which can form intramolecular hydrogen bonds are less strongly adsorbed than those which cannot.

[8] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 307.

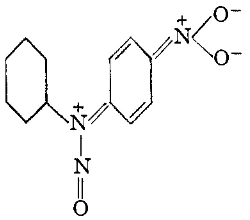
[9] Ref. 8, p. 222.

because in both the 2-nitro group is internally compensated. The stronger affinity of VIII derives from the ability of a 4-nitro group in an unsubstituted ring to withdraw from the ring more nearly its normal proportion of electrons. Thus it bonds more strongly than the 4-nitro group in VI which because of the chelation in the same ring is prevented from withdrawing its normal complement of electrons.

The effect of 4-nitro substitution into N-nitroso compounds will be considered in the next section in conjunction with 2-nitro substitution into N-nitroso compounds and the related subject of N-nitrosation of 2-nitro and 4-nitro derivatives.

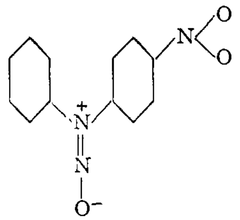
2-Nitro and 4-Nitro Substitution into N-Nitroso Compounds and N-Nitrosation of 2-Nitro and 4-Nitro Compounds (Conditions No. 4, 8, 9 and 10).—Nitration of N-nitrosodiphenylamine (III) in either the 2 or 4 position results in compounds of increased adsorption affinity (VII and IV) but this is the only environment in which the introduction of a 2-nitro group has a greater effect than that of a 4-nitro group. Compounds IV and VII may also be considered as N-nitrosation products of 4-nitrodiphenylamine (X) and 2-nitrodiphenylamine (II), respectively. In this instance, N-nitrosation of the 4-nitro compound (X) has produced a decrease in affinity whereas that of the 2-nitro compound (II) has resulted in an increase.

The reasons for the observed effects of N-nitrosation are obvious: in II, it breaks the intramolecular hydrogen bond which causes weak affinity whereas in X, it disrupts the effective combination which produces unusually strong affinity. The unusual feature, however, is the fact that VII which contains a 2-nitro group is more strongly adsorbed than IV which has a 4-nitro group. The cause probably lies in steric factors which influence the resonance forms of IV and VII. Compound IV can easily be coplanar and hence resonate between such structures as



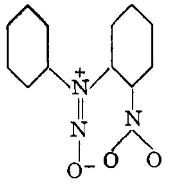
IVa

and

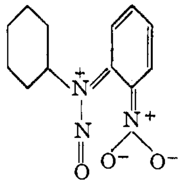


IVb

although no estimate of the importance of either structure may be made. In VII, however, steric effects of the nitro and nitroso groups probably prevent the nitro group from being coplanar with the ring and hence forms such as VIIa should be more prominent than such structures as VIIb.



VIIa



VIIb

Hence, if the nitroso group determines adsorption, VII should be the more strongly adsorbed. It may, of course, be that in addition to the above the proximity of the two groups in VII coincides especially well with the spatial arrangements of the adsorbent and thus permits two good bonds to be formed whereas spatial conditions may be less satisfactory between IV and the adsorbent so that only one good or two weak bonds result.

Other 2-Nitro Substitutions (Conditions No. 6 and 7).—It is not surprising that the introduction of a 2-nitro group into a 4-nitro derivative (Condition 6) should result in a decrease in affinity. This condition is related to 2 and 3 which have been discussed above.

The substitution of a second 2-nitro group into the molecule produces a greater increase than the first but one somewhat less than that of a 4-nitro group. (Compare I → II with II → V and V → XII with VI or VIII → XII.) The greater effect of the second 2-nitro group may be ascribed to one of two causes: either the strong intramolecular hydrogen bond of the first 2-nitro group permits little or no intramolecular bonding of the second group and thus allows it to bond to the adsorbent, or both may partake equally in intramolecular hydrogen bonding which then is weaker to either group and allows stronger bonding to the adsorbent than when only one 2-nitro group is present. The lesser effect of a second 2-nitro group as compared to a 4-nitro group probably is caused by steric conditions which prevent coplanarity.

Conclusions.—The relationships which have been discussed are applicable as the number of substituent groups in the molecule is multiplied but although this is true, no evidence can be adduced to show whether the increase in adsorption in a series such as II → VIII → XIII is due to increase in the number of hydrogen bonds between the molecule and the adsorbent or to the influence of several groups upon one group with a consequent augmenting of bonding strength to that one group.

This discussion has not considered the obviously important factor of the structure of the adsorbent in influencing adsorption affinity. This factor cannot be taken into account because no information about the spatial relationships of the adsorbent is available.

N-Ethylaniline and Derivatives.—Table III lists the relative adsorption affinities of N-ethylaniline and some of its derivatives. Certain

TABLE III

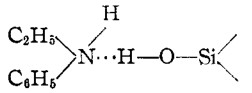
RELATIVE ADSORPTION AFFINITIES OF DERIVATIVES OF N-ETHYLANILINE ON SILICIC ACID–CELITE[a]

N-Nitroso-2-nitro-N-ethylaniline (XXV)—most strongly adsorbed
4-Nitro-N-ethylaniline (XXIV)
2,4-Dinitro-N-ethylaniline (XXIII)
N-Nitroso-4-nitro-N-ethylaniline (XXII)
N-Nitroso-N-ethylaniline (XXI)
N-Ethylaniline (XX)
2-Nitro-N-ethylaniline (XIX)—least strongly adsorbed

[a] Mixtures of benzene and ligroin or ether and ligroin were the developers.

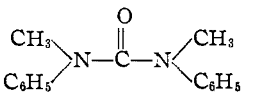
differences in this series relative to that of diphenylamine should be noted: N-ethylaniline is more strongly adsorbed than diphenylamine; a derivative is less strongly adsorbed than the parent of the series (XIX and XX as compared to I and II); and XXIV and XXV should be inverted in position to be comparable to the diphenylamine series.

The explanation of these differences probably lies in the greater basicity of N-ethylaniline and hence its more negative nitrogen atom which in the case of N-ethylaniline itself would cause stronger affinity by permitting stronger bonding of the type

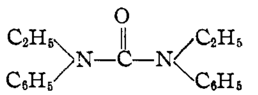


Application to Non-nitrated Compounds.—Because of the qualitative nature of the principles which have been advanced to explain the observed adsorption series, it is necessary to limit the consideration to the relationships of closely similar compounds. Until now we have discussed only the relationships of compounds which differ by relatively polar groups, which groups offer abundant opportunity for hydrogen bonding. However, information is available concerning the relative adsorption affinities on silicic acid of other compounds some of which do not differ in this way. It is interesting to extend the present discussion to some of them in order to obtain an idea of the modification which may be necessary for its further extension.

Two derivatives of urea whose structures are



methyl centralite (XXVI)



centralite (XXVII)

are readily separable on silicic acid when developed with 1:9 ether–ligroin (by volume); methyl centralite is the more strongly adsorbed. Since the electronic structures of these compounds probably are essentially the same, principles other than those which govern the relative affinities of the compounds previously considered must be sought. Hydrogen bonding to these compounds must occur at the carbonyl oxygen or the amide nitrogens and the strength of the hydrogen bond would seem to be conditioned by the ability of the anchoring groups of the molecule to approach the adsorbent, that is, by the steric conditions around the anchoring groups. If models of these molecules are made in which normal bond lengths, bond angles and van der Waals radii are used, the various possible dispositions of the alkyl and aryl groups in no way seem to affect the ability of the carbonyl oxygen to approach the adsorbent. However, the two additional methyl groups of centralite seem to prevent the same closeness of approach of the nitrogen atoms to the adsorbent that is possible with methyl centralite. The significance of this difference is difficult to assess in the absence of a model of the adsorbent. The relative adsorption affinities of these compounds and of those of compounds more or less closely related to them are shown in Table IV. For certain closely related pairs such as those

TABLE IV

RELATIVE ADSORPTION AFFINITIES OF SOME SUBSTITUTED UREAS, URETHANS AND FORMAMIDES

1,1-Diphenylurea (XXVIII)—most strongly adsorbed
1,1-Diphenyl-3,3-dimethylurea (XXIX)
1,1-Diphenyl-3,3-diethylurea (XXX)
(1,3-Diphenyl-1,3-dimethylurea(methylcentralite)(XXVI)
1,3-Diphenylurea (carbanilide) (XXXI)
(1,3-Diphenyl-1,3-diethylurea (centralite) (XXVII)
N,N-Diphenylformamide (XXXII)
N-Methyl-N-phenylurethan (XXXIII)
N-Ethyl-N-phenylurethan (XXXIV)
N-(*o*-Tolyl)-urethan (XXXV)
N-(*p*-Tolyl)-urethan (XXXVI)
(N,N-Diphenylurethan (XXXVII)—least strongly adsorbed

TABLE V

DEVELOPERS FOR DERIVATIVES OF DIPHENYLAMINE AND N-ETHYLANILINE AND FOR SOME MISCELLANEOUS COMPOUNDS

Compound	Ratio benzene–ligroin[a]	% Ether in ligroin[a]	% Ether in benzene
I	1:4		
II	1:4		
III	1:4		
IV	1:3		
V	...[b]		
VI	1:2		
VII	2:3		
VIII	1:1		
IX	1:1		
X	1:1		
XI			
XII	3:1		
XIII	3:1		
XIV	4:1		
XV	1:0		
XVI	...[c]		
XVII	...[c]		
XVIII	...[c]		
XIX	1:4	0.5	
XX		1	
XXI	1:3	2	
XXII	1:1	5	
XXIII	1:1	10	
XXIV	1:0	13	
XXV		18	0.5
XXVI		10	
XXVII		10	
XXVIII		100	
XXIX		50	10
XXX			5
XXXI			3
XXXII			0.5
XXXIII	1:0	2	
XXXIV		2	0.5
XXXV			0.5
XXXVI			0.5
XXXVII			0.5

[a] The ratios and percentages are by volume. [b] If no value is given, the type of developer is not the best available. However, a developer in the proportion that was used for similarly adsorbed compounds would be suitable. Values for ether in ligroin or benzene are not given for diphenylamine derivatives because the discussion is based upon the affinities in benzene–ligroin. [c] 10% acetone in ligroin is suitable.

which are bracketed, arguments which have been given for centralite and methyl centralite apply, but broader generalizations on the basis of steric hindrance are more difficult to defend.

Experimental[10]

Materials.—A mixture of Merck and Co., Inc., Reagent Silicic Acid and Celite 535 (2:1 by weight) which had been prewashed with *V* ml.[11] of ether and 2 *V* ml. of ligroin (60–70°) was used as the adsorbent in all experiments; the size of the column usually was 19 × 150 mm. Further information about the adsorbent, the solvents, most of the compounds which were chromatographed, and the reagents for the detection of colorless zones has already been presented.[2,3,4]

Methods.—The adsorption sequences were obtained by the following general method. A compound was placed on the column in a solvent whose developing properties were as weak as possible and then was developed with a developer which was expected to be satisfactory. On the basis of the results, other chromatograms were run in which the composition of the developer was changed until the most satisfactory one of each of several solvent mixtures had been found. Mixed chromatograms with similarly adsorbed compounds were then made in order to determine the exact sequence. Sometimes separation of two similarly adsorbed compounds into discrete zones could not be achieved with the developers which were used to establish the sequences given. When such was the case, the sequence was determined by running separate chromatograms of each compound and measuring the position of the zone after the passage of a given quantity of developer. Unless the column was overloaded, all evidence showed that a zone moved in the same manner when a mixture was present as it did when the compound was chromatographed alone.

Developing Mixtures.—Table V gives the solvent mixtures which develop compounds in the same series at similar rates. It should be mentioned again that these mixtures must only be considered approximate because silicic acid shows variations from lot to lot as was amply found in these experiments and further studied by Trueblood and Malmberg.[12]

Acknowledgment.—Most of the experimental work was done by Laura L. Fong, Charlotte Green, Earl Hoerger, Richard M. Lemmon, Earl W. Malmberg, Rene Mills, Kenneth N. Trueblood and M. Kent Wilson. I wish to thank Professors Linus Pauling, Robert B. Corey, Verner Schomaker and L. Zechmeister and Dr. Kenneth N. Trueblood for critical and stimulating discussions.

Summary

The unexpected relative adsorption affinities which are shown by nitro and nitroso derivatives of diphenylamine and N-ethylaniline on silicic acid columns have been correlated with the strength of the hydrogen bonds between the adsorbed compound and the adsorbent. The strength of the hydrogen bonds is conditioned by such features as intramolecular hydrogen bonding, the contribution of various resonance structures of the molecule and the effect of other groups upon such resonance structures.

Some of the applications and limitations of this theory are illustrated and discussed.

PASADENA 4, CALIFORNIA RECEIVED APRIL 10, 1950

---

[10] The experimental work was done for the Office of Scientific Research and Development under Contracts OEMsr-702 and OEMsr-881 with the California Institute of Technology.

[11] *V* ml. is the volume of solvent which is required to wet completely the column of adsorbent.

[12] K. N. Trueblood and E. W. Malmberg, *Anal. Chem.*, **21**, 1055 (1949).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Rate of Oxime Formation of Isomeric Ketones from *p*-Cymene[1]

BY MARY J. CRAFT[2] AND CHAS. T. LESTER[3]

In a previous communication[4] we have described the medium and method for measuring the rate of oxime formation of alkyl phenyl and alkyl *p*-xylyl ketones. We have extended this method to include the isomeric ketones containing the carvacryl (2-methyl-5-isopropylphenyl) and the thymyl (3-methyl-6-isopropylphenyl) groups.

Preparation of Carvacryl Ketones.—These ketones were prepared on a 1 molar scale according to a standard procedure.[5] They are unusually difficult to purify due to a pronounced tendency to superheat. Some samples were fractionally distilled as many as four times. The ketones are listed in Table I. The physical properties are those of samples used in the rate determinations.

Preparation of Thymyl Ketones.—These ketones were prepared on a 0.3 molar scale by the reaction of 3-methyl-6-isopropylbenzoyl chloride with a suitable dialkylcadmium compound.[6] The 3-methyl-6-isopropylbenzoyl chloride was prepared from thymol as previously described.[7] The ketones were purified by two fractional distillations. The properties listed in Table II are those of the center cut fractions used in the rate determinations.

Determination of Rates of Reaction.—The medium and method is that previously described. Glass electrode readings of *p*H values indicated that the medium had been properly buffered to correspond to previous conditions. The carvacryl ketones were measured in a solution 0.1 *M* in ketone and 0.1 *M* in hydroxylamine hydrochloride; the thymyl ketones were measured in a solution 0.1 *M* in ketone and 0.2 *M* in hydroxylamine hydrochloride. Duplicate values were determined and checked within 5% in all cases. The reactions were carried to 70% completion or better and the *k* values calculated by the method of least squares. The rates were measured in a bath with a temperature variation of ±0.05°. The results obtained at 30, 35 and 40° are included in Table III.

---

[1] This work was made possible by a contract with the Office of Naval Research.

[2] Taken from the Ph.D. Thesis of Mary J. Craft, Emory University, 1950.

[3] Responsible co-author.

[4] Suratt, Proffitt and Lester, THIS JOURNAL, **72**, 1561 (1950).

[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[6] Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

[7] Lester and Bailey, THIS JOURNAL, **68**, 375 (1946).