Figs. 4 and 11). For some of their results they found the following equation to hold

$$\frac{k_1}{k_2} = \left(\frac{C_{\mathrm{Pt},\,1}}{C_{\mathrm{Pt},\,2}}\right)^b$$

The experiments reported here indicate a fundamental difference in the action of acids and of salts on platinum and gold sols. They indicate that acids (or hydrogen ion) may be adsorbed in a manner similar to iodine and other substances of molecular or ionic nature; in sufficiently high concentration they coagulate the colloid by virtue of their ionic charges much as salts do. If the salts can be said to be adsorbed, it seems to be another type of adsorption which has relatively little effect on the portion of the surface active in catalysis.

The role played by the particle size of the colloid is rather obscure. Gold sol II showed a much greater catalysis per unit of gold than sol I in spite of the greater acidity; this was presumably due to greater dispersion of the gold. On the other hand, coagulation would be expected to decrease the surface area, but it seems that the initial coagulation may actually lead to a temporarily greater active surface.

The author takes this opportunity to express his gratitude to Professor J. N. Brönsted, who suggested this work and whose interest and aid made possible its completion.

Summary

Colloidal and finely divided platinum and gold have been shown to have a pronounced catalytic effect on the decomposition of nitramide in aqueous solution. In suitable solutions 10^{-6} g./cc. of these metals may increase the normal decomposition rate two to ten times. The platinum sols used were more active catalysts than the gold sols, but the activity varies a great deal with the history of the individual sol and especially its content of acids and other reagents.

The mechanism of the catalysis has been explained as a rapid decomposition of nitramide adsorbed by colloidal particles. The effect of "poisons," including strong acids, iodine, dextrin and glucose has been explained as due to preferential adsorption with displacement of the nitramide. The colloidal metal catalysis has been shown to resemble similar catalysis of hydrogen peroxide decomposition.

NEW YORK, N. Y.
COPENHAGEN, DENMARK RECEIVED NOVEMBER 2, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF YALE UNIVERSITY]

Viscosity and Chemical Constitution

BY MOTT SOUDERS, JR.[1]

Previously, the most successful attempts to define relationships between the viscosity and the chemical constitution of organic liquids have been based on comparisons at constant temperature,[2] at the temperature of equal viscosity–temperature slope,[3] or at equal fluidity.[4] These restrictions have made viscosity comparisons difficult and have limited seriously the usefulness of the relationships between viscosity and chemical constitution.

Viscosity Density Constant.—For a wide range of organic liquids, plotting the logarithm of the logarithm of the viscosity at constant pressure (in millipoises) against the density (in grams per cc.) gives substantially a straight line for each compound. The curvature usually increases in the vicinity of the melting point or boiling point, but over the intermediate range the function is nearly linear. An examination of such plots for a large number of compounds shows that although the slopes vary widely among the different liquids, the intercepts are nearly equal so that an average value of -2.9 may be used for all organic liquids. These observations lead to a general viscosity–density equation

$$\log_{10}(\log_{10}\eta) = md - 2.9 \qquad (1)$$

in which η is viscosity in millipoises at atmospheric pressure; m is a constant characteristic of each liquid; and d is density in grams per cc.

Although an equation of the general type

$$\eta = Ae^{Be^{Cd}} \qquad (2)$$

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[1] Sterling Fellow in Chemical Engineering.

[2] Dunstan and Thole. "The Viscosity of Liquids," Longmans. Green and Company, London, 1914, p. 36.

[3] Thorpe and Rodger, *Phil. Trans.*, **A185**, 397 (1894); *Proc. Roy. Soc. (London)*, **A60**, *152 (1896)*.

[4] Bingham and Harrison, *Z. physik. Chem.*, **66**, 1 (1909); E. C. Bingham, THIS JOURNAL, **33**, 302 (1910).

may be derived from kinetic reasoning, it appears more acceptable at present to regard equation (1) as being essentially empirical.

The viscosity–density constant, *m*, of equation (1), has been calculated for most of the organic liquids for which adequate viscosity and density data are available. The results for the temperature range between 0 and 60°, including a wide variation in viscosity and density among the various compounds, are reported in Table II. From this table it may be seen that the value of *m*, as calculated by equation (1), is substantially a constant for each liquid in nearly all cases. A few liquids, notably water and phenol, do not follow the linear equation (1) and in these cases any calculated value for *m* is purely arbitrary.

Viscosity–Constitutional Constant.—The fact that the values of *m* for all the paraffin hydrocarbons are nearly equal suggests a relationship between the viscosity–density constant, *m*, and the chemical constitution of organic liquids. This relationship is

$$mM = I \qquad (3)$$

in which *m* is viscosity–density constant from equation (1); *m* is molecular weight; *I* is viscosity–constitutional constant.

The viscosity–constitutional constant, *I*, obtained from observed viscosity and density and equations (1) and (3) should agree with a calculated value of *I* obtained from the summation of general atomic and structural constants.

Beginning with values for the CH_2 group and hydrogen atom obtained from the paraffin hydrocarbons, a number of atomic and structural constants have been derived and are presented in Table I. Values for hydrogen, carbon, oxygen, and hydroxyl group, and for double bond, six-carbon ring, and side groups on a six-carbon ring appear to be well established. Some of the other values are based on more limited data and may require revision.

From the data on 117 organic liquids, Table II,

TABLE I

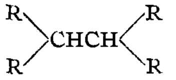
ATOMIC AND STRUCTURAL CONSTANTS

Atomic and group values

CH_2	+55.6	OH	+57.1	N	+37
H	2.7	COO	90	Cl	60
C	50.2	COOH	104.4	Br	79
O	29.7	NO_2	80	I	110

Structural values

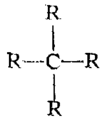
Double bond −15.5

 +8

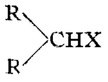
—CH=CHCH$_2$X +4

5-C ring −24
6-C ring −21

Side group on 6-C ring

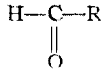
 +13

$R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-R$

 +6

in which X is a negative group

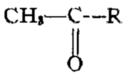
Mol. wt. less than 17 = −9

 +16

$H-\underset{\displaystyle O}{\underset{\|}{C}}-R$

Mol. wt. more than 16 = −17

Ortho and para = +3
Meta = +1

 +5

$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-R$

TABLE II

Compound	Viscosity–density constant at temp., °C. 0	20	40	60	*I* Obsd.	Calcd.
n-Pentane	3.961	3.935			283–285	283.4
n-Hexane	3.956	3.949	3.940		339–341	339.0
n-Heptane	3.934	3.933	3.931	3.922	393–394	394.6
n-Octane	3.937	3.937	3.939	3.936	449	450.2
n-Nonane	3.946	3.941	3.940	3.942	505	505.8
n-Decane	3.950	3.944	3.943	3.946	561	561.4
n-Undecane	3.956	3.951	3.953	3.956	617	617.0
n-Dodecane		3.954			673	672.6
n-Heptadecane			3.98		956	950.6

TABLE II (*Continued*)

Compound	Viscosity-density constant at temp., °C.				I	
	0	20	40	60	Obsd.	Calcd.
Isopentane	3.973	3.943			283–286	283.4
Isohexane		3.944			340	339.0
3-Methylpentane		3.921			338	339.0
Diisopropyl	4.035	4.032			347	347.0
2,2-Dimethylbutane		4.092			352	352.0
Isoheptane	3.926	3.923			393	394.6
Isoprene		3.562			242	241.6
Diisopropenyl (diallyl)		3.718			305	305.2
Cyclopentane		3.62			254	254.0
Cyclohexane		3.716	3.716		312.5	312.6
Methylcyclohexane		3.69			362	359.2
Octadecylcyclohexane			3.89		1309	1296
Docosylcyclohexane			3.915		1536	1519
5-Cyclohexyldocosane			3.91		1534	1519
5-Cyclohexylhexacosane			3.96		1776	1741
Benzene	3.201	3.197	3.203	3.202	249.8	249.9
Toluene	3.220	3.218	3.219	3.219	296.2	296.5
Ethylbenzene		3.249			344.7	344.1
o-Xylene		3.268			347	346.1
m-Xylene	3.241	3.238	3.236	3.235	343–344	344.1
p-Xylene		3.262			346	346.1
Octadecylbenzene			3.76		1242	1234
Docosylbenzene			3.82		1476	1456
5-Phenyldocosane			3.82		1476	1456
5-Phenyl-5-docosene			3.74		1437	1435
5-Phenylhexacosane			3.87		1712	1678
5-Phenyl-5-hexacosene			3.79		1670	1657
Naphthalene					376.6	376.6
β-Octadecylnaphthalene			3.64		1385	1362
β-Docosylnaphthalene			3.71		1619	1585
β-Hexylnaphthalene			3.29		698	695
Methyl alcohol	3.529	3.522	3.510		112–113	115.4
Ethyl alcohol	3.717	3.716	3.709		117	117.0
n-Propyl alcohol	3.785	3.773	3.758	3.746	225–227	226.6
Isopropyl alcohol	3.881	3.871	3.840		230–233	232.6
n-Butyl alcohol	3.806	3.788	3.768		279–282	282.2
Isobutyl alcohol		3.857	3.846	3.832	283–285	282.2
2-Ethyltetradecanol		3.940	3.914	3.895	944–954	949
2-Heptylnonanol		3.960	3.932	3.910	947–959	949
Allyl alcohol		3.460			200.9	205.7
Cyclohexanol			3.498	3.457	346–350	350
Phenol			2.954	2.930	275–278	287.2
Acetone	3.293	3.299	3.301		191–192	191.0
Methyl ethyl ketone	3.354	3.350	3.352	3.351	241.5	241.6
Diethyl ketone	3.346	3.347	3.351		288–289	292.2
Methyl propyl ketone	3.400	3.401	3.405		293	297.2
Cyclohexanone		3.202	3.203	3.203	314	315.1
Acetaldehyde		3.13			138	140.4
Propionaldehyde		3.28			191	191
Ethyl ether	3.476	3.462			257	257.5
Methyl propyl ether	3.47				257	257.5
Ethyl propyl ether	3.55				313	313.1
Ethyl isobutyl ether		3.64			372	368.7
n-Propyl ether		3.62			370	368.7

TABLE II (*Concluded*)

Compound	Viscosity-density constant at temp., °C.				*I*	
	0	20	40	60	Obsd.	Calcd.
Acetic acid		2.798	2.800	2.811	168–169	167.7
Propionic acid		2.94			218	218.3
n-Butyric acid		3.104	3.112	3.123	273–275	273.9
Isobutyric acid		3.11			274	273.9
n-Valeric acid		3.23			330	329.5
n-Caproic acid		3.33			387	385.1
Methyl formate	2.694	2.703			161–162	161
Ethyl formate	2.898	2.907	2.916		215–216	216.6
n-Propyl formate	3.033	3.040	3.047	3.054	267–269	272
Methyl acetate	2.849	2.854	2.860		211–212	211.6
Ethyl acetate	3.010	3.015	3.020	3.026	265–266	267.0
n-Propyl acetate	3.146	3.140	3.146	3.153	321–322	322.8
2-Ethyltetradecyl acetate	3.693	3.681	3.672	3.668	1043–1049	1041
2-Heptylnonyl acetate	3.710	3.686	3.673	3.670	1043–1054	1041
Methyl propionate	2.966	2.971	2.977	2.983	261–263	262
Ethyl propionate	3.096	3.103	3.110	3.118	316–318	317.8
Methyl *n*-butyrate	3.092	3.096	3.102	3.108	316–317	317.8
Methyl isobutyrate	3.093	3.098	3.106	3.112	316–317	317.8
Aniline		3.05			284	280.6
Methylaniline		3.07	3.06		328–329	328.2
Benzylamine		3.05			326	328.2
Ethylaniline		3.15			381	383.8
Dimethylaniline		3.19			386	383.8
o-Toluidine			3.10		332	330
p-Toluidine			3.11		333	330
Nitrobenzene	2.514	2.514	2.504		308–309	310.2
m-Nitrotoluene		2.622	2.617	2.616	358.9	351.8
n-Propyl chloride		2.96			232	229.5
Isopropyl chloride		3.04			238	235.5
Allyl chloride		2.79			213	212.6
Isobutyl chloride		3.09			286	285.1
Chlorobenzene	2.580	2.581	2.584	2.587	290–291	290.2
o-Chlorotoluene		2.68			339	339.8
m-Chlorotoluene		2.68			339	337.8
p-Chlorotoluene		2.69			340	339.8
Dichloromethane	2.01	2.03			171–172	175.6
Ethylene chloride	2.28	2.285	2.295	2.307	226–228	231.2
1,1-Dichloroethane		2.33			231	231.2
Ethyl bromide	1.820	1.831			198–199	192.9
n-Propyl bromide		2.03			250	248.5
Isopropyl bromide		2.09			257	254.5
Allyl bromide		1.96			237	231.6
Isobutyl bromide		2.21			303	304.1
Bromobenzene		1.956	1.958	1.962	307–308	309.2
o-Bromotoluene		2.09			357	358.8
m-Bromotoluene		2.085			356	356.8
p-Bromotoluene			2.094	2.095	358	358.8
Methyl iodide		1.20			170	168.3
Ethyl iodide	1.431	1.439	1.448	1.459	223–228	223.9
n-Propyl iodide	1.619	1.625	1.633		275–278	279.5
Isopropyl iodide	1.649	1.654	1.666		280–283	285.5
Allyl iodide	1.54	1.55			259–260	262.6
Isobutyl iodide		1.79			329	325.1
Iodobenzene		1.633	1.635	1.636	333–334	340.2

a comparison has been made between the observed and calculated values of the viscosity–constitutional constants, *I*. It may be seen that in nearly all cases the differences are less than 1%. As a group, the halogen substituents appear to produce the greatest discrepancies between the observed and calculated values.

Accumulation of Negative Groups.—When there is an accumulation of negative groups in the molecule, particularly if attached to adjacent carbon atoms, the calculated value of I is considerably more than the observed value. This fact, as shown by Table III, indicates that an additional negative "strain-constant" is required. Better data on such compounds and further study are required before it may be determined whether adequate "strain-constants" can be derived.

TABLE III

ACCUMULATION OF NEGATIVE GROUPS

Compound	I, obsd.	I, calcd.	Diff.
Chloroform	221–226	232.9	+ 7
Carbon tetrachloride	278–282	303.2	+23
Tetrachloroethylene	296–299	324.9	+27
1,1,2,2-Tetrachloroethane	316–318	345.8	+29
Trichloroethylene	250	267.6	+18
Pentachloroethane	366	403.1	+37
Dibromomethane	212	213.6	. .
Bromoform	264	289.9	+16
Ethylene bromide	257–259	269.2	+11
1,2-Dibromopropane	311	324.8	+14

Summary

1. An equation relating viscosity and density, $\log_{10}(\log_{10}\eta) = md - 2.9$, is found to fit the data on 117 organic liquids.

2. The viscosity–density constant, m, is characteristic of each liquid and when multiplied by molecular weight becomes a constitutive property, I, of each compound.

3. Values of atomic and structural constants are derived from which the viscosity–constitutional constant, I, may be calculated.

4. Comparison of the observed and calculated values of I for 117 organic liquids indicates, in nearly all cases, errors of less than 1%.

NEW HAVEN, CONN. RECEIVED NOVEMBER 10, 1937

α-Aryl-β-dialkylaminoalkyl Ureas as Local Anesthetics

BY HENRY WENKER

Since compounds which contain an aromatic nucleus combined, by means of an electronegative group, with a dialkylaminoalkyl radical, often possess local anesthetic properties, the preparation of some ureas to which the above description applies, seemed of interest. Only one compound of this class has been described hitherto.[1]

The ureas under consideration were prepared by the action of an aryl isocyanate with an *as*-dialkyl alkylenediamine. The isocyanates used were phenyl-, *o*-methoxyphenyl-, *p*-ethoxyphenyl isocyanate and phenyl isothiocyanate; the amines used were 1-piperidino-2-aminopropane and 1-di-*n*-butylamino-2-aminopropane. The ureas, as far as they were obtained in crystalline form, are described in the table.

Experimental

Piperidine and di-*n*-butylamine, respectively, were combined in the usual manner with propylene oxide. Of the resulting amino alcohols the former is known;[2] the latter, obtained in 84% yield, forms a colorless liquid boiling at 130° (15 mm.).

Anal. Calcd. for $C_{11}H_{25}NO$: N, 7.5. Found: N, 7.4.

The hydrochlorides of the amino alcohols were allowed to react with a 50% excess of thionyl chloride for twenty-four hours at room temperature and the excess of thionyl chloride was then removed by gentle heating *in vacuo*. The crude hydrochlorides of the β-chloropropyl bases were used for the following reaction; a sample of the well-crystallized N-(β-chloropropyl)-piperidine hydrochloride, however, was crystallized from amyl acetate. It forms long needles melting at 204°.

Anal. Calcd. for $C_8H_{17}NCl_2$: Cl, 36.0. Found: Cl, 36.2.

No.	Urea	Formula	M. p., °C.	N, % Calcd.	N, % Found
1	α-Phenyl-β-(1-piperidinopropyl-2)	$C_{15}H_{23}ON_3$	149	16.1	16.1
2	α-(*o*-Methoxyphenyl)-β-(1-piperidinopropyl-2)	$C_{16}H_{25}O_2N_3$	135	14.4	14.6
3	α-(*p*-Ethoxyphenyl)-β-(1-piperidinopropyl-2)	$C_{17}H_{27}O_2N_3$	124	13.8	13.6
4	α-Phenyl-β-(1-piperidinopropyl-2)-thio	$C_{15}H_{23}SN_3$	123	15.2	15.2
5	α-Phenyl-β-(1-di-*n*-butylaminopropyl-2)	$C_{18}H_{31}ON_3$	113	13.8	13.9
6	α-(*o*-Methoxyphenyl)-β-(1-di-*n*-butylaminopropyl-2)	$C_{19}H_{33}O_2N_3$	94[a]	12.2	12.1

[a] The melting point may be low, as the compound crystallized difficultly.

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(1) Ristenpart, *Ber.*, **29**, 2527 (1896).

(2) German Patent 547,174 (1927).