cule transforming chemically unreactive groups to chemically active ones.

Extensive unfolding of the peptide chains of native proteins caused by the breaking up of intramolecular hydrogen bonds is known to take place in the presence of denaturing agents such as urea and guanidine.[1] Such a far reaching change in the configuration of the protein molecule would explain the result obtained where in the presence of guanidine at *p*H 10 most of the disulfide bonds of each of the three proteins investigated were reduced.

The respective *p*H ranges at which human and bovine serum albumin and bovine γ-globulin were found to have a minimal number of disulfide bonds available for reduction correspond to those *p*H ranges where these proteins are known to have a relatively small net electrical charge. Increasing the acidity or alkalinity beyond this *p*H range led to an increase in the number of disulfide bonds reduced. This suggests that increasing the net electrical charge leads to some unfolding of the protein molecule due to electrostatic repulsion thereby exposing a few disulfide bonds to reduction. The observed reversal of the number of disulfide bonds available for reduction implies that the change in configuration of bovine serum albumin in the *p*H range 1.2 to 10.2 (see Table I) and of bovine γ-globulin in the *p*H range 5.0 to 10.2 are reversible.

Similarly, other investigators have concluded that bovine serum albumin can undergo reversible configurational changes within limited *p*H ranges. Klotz, *et al.*,[16] observed that the binding of anionic dyes by this protein is reversible and increases from *p*H 6.8 to 9.2. This was explained as being due to a reversible change in the intramolecular bonding of the protein leading to the exposure of new side chains capable of interaction within the specific dye molecules. Tanford[17] found that the electrostatic interaction factor *w* decreases for bovine serum albumin from *p*H 5.0 to 2.5. The decrease in *w* was interpreted to be the result of a corresponding increase in the radius of the molecule. Champagne and Sadron[18] measured the viscosity and diffusion of bovine serum albumin over the *p*H range 3.5 to 10.0. From the data obtained they concluded that the shape of the molecule undergoes a reversible change from a sphere at its isoelectric point, *p*H 5.3, to an elongated ellipsoid of revolution in the *p*H ranges 5.3 to 3.45 and 5.3 to 7.4.

The curves in Fig. 2 show that bovine γ-globulin in contrast to human and bovine serum albumin already exists in a partially unfolded state at physiological *p*H. This may somehow be related to the immunological functions of the γ-globulins.

(16) I. M. Klotz, R. K. Burkhard and J. M. Urquhart, *J. Phys. Chem.*, **56**, 77 (1952).

(17) C. Tanford; T. Shedlovsky, Editor, "Electrochemistry in Biology and Medicine," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 248.

(18) M. Champagne and C. Sadron, "Simposio Internazionale di Chimica Macromoleculare," Supplemento a "La Ricerca Scientifica," Anno 25°, 1955, p. 3.

REHOVOTH, ISRAEL

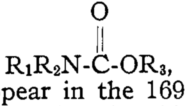
[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

The Carbonyl Absorption of Carbamates and 2-Oxazolidones in the Infrared Region

BY S. PINCHAS AND D. BEN-ISHAI

RECEIVED JANUARY 28, 1957

The data for the C=O frequency in 21 carbamates show that each type of a carbamic group has its own characteristic absorption region. Primary carbamates, both in the solid phase and in solution in chloroform, absorb at 1725 ± 3 cm.$^{-1}$. Secondary carbamates absorb at 1705–1722 and tertiary at 1687 ± 4 cm.$^{-1}$. The C=O frequency of the carbamic group in linear carbamates with a cyclic nitrogen atom depends upon the electronic effects of the ring and its substituents. Fourteen 2-oxazolidones showed their cyclic carbamic C=O frequency at 1746–1810 cm.$^{-1}$. An appreciable absorption band at 1029–1059 cm.$^{-1}$ is characteristic for the 2-oxazolidone ring.

Although the carbonyl absorption band of the carbamates,  $R_1R_2N\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR_3$, has already been reported to appear in the 1690–1736 cm.$^{-1}$ region,[1] only two exact values for this frequency in the case of simple carbamates could be found in the literature[2] these being 1661 cm.$^{-1}$ for an oil paste of ethyl carbamate (urethan) and 1706 cm.$^{-1}$ for a liquid layer of ethyl N-methylcarbamate (methylurethan). Recently the carbonyl frequency of various esters of phenylcarbamic acid (phenylurethans) was measured[3] and was also found to be in this region being about 40 cm.$^{-1}$ higher than in anilides.

Since simple amides can usually be recognized as primary, secondary or tertiary amides from the frequency of their C=O stretching vibration in dilute non-polar solutions, this frequency appearing at about 1690, 1680 and 1650 cm.$^{-1}$, respectively,[4] it was interesting to see whether a parallel regularity could also be found for the similar carbamates. In view of the already mentioned lack of data for the carbonyl frequency in individual simple carbamates, their measurement seemed worth while and, since a series of such compounds was at our disposal, this measurement was undertaken.

Table I summarizes the results obtained for the carbamic carbonyl group frequency in 21 various carbamates.

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(1) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen & Co., London, 1954, p. 191; (b) H. Thompson, D. Nicholson and L. Short, *Discussions Faraday Soc.*, **9**, 229 (1950).

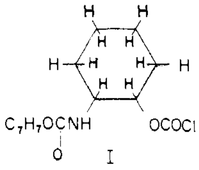
(2) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, pp. 157–159.

(3) (a) N. F. Hayes, R. H. Thomson and M. St. C. Flett, *Experientia*, 11, 61 (1955); (b) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428(1956).

(4) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

TABLE I

THE INFRARED FREQUENCY OF THE CARBAMIC CARBONYL GROUP STRETCHING VIBRATION IN VARIOUS CARBAMATES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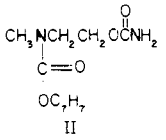
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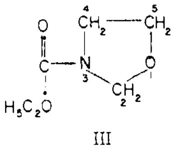
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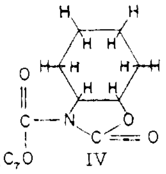
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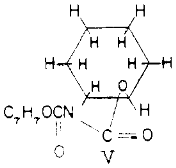
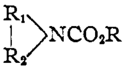
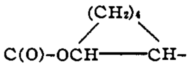
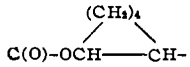

V

No.	Material	R	R_1	R_2	Concn., g.	+ ml.	Frequency, cm.$^{-1}$
	Primary carbamates: NH_2COOR						
1	Ethyl carbamate	C_2H_5	......	......	0.21	1 $CHCl_3$	1725
					Oil paste		1728
2	Benzyl carbamate	C_7H_7	......	......	.04	1 $CHCl_3$	1724
3	2-Aminoethyl carbamate hydrobromide	$CH_2CH_2NH_2HBr$	......	......	Oil paste		1726
4	2-Carbobenzyloxyaminoethyl carbamate	$CH_2CH_2NHCOOC_7H_7$	......	......	Low and unknown: in $CHCl_3$		1718
	Secondary carbamates: NHR_1COOR						
5	N-Carboxyglycine dibenzyl ester	C_7H_7	$CH_2COOC_7H_7$	......	0.12	1 $CHCl_3$	1714
					Oil paste		1715
6	Ethyl N-(2-hydroxyethyl)-carbamate	C_2H_5	CH_2CH_2OH	......	0.043	1 CCl_4	1705
7	N_1-Carbobenzyloxyglycine-N_2-(2-chloroethyl)-amide	C_7H_7	$CH_2CONHCH_2CH_2Cl$	......	In $CHCl_3$		1715[a]
8	2-Carbobenzyloxyaminocyclohexylchlorocarbonate (I)	C_7H_7	$C_6H_{10}OCOCl$	......	0.11	1 $CHCl_3$	1722[b]
	Tertiary carbamates: NR_1R_2COOR						
9	Ethyl dimethylcarbamate	C_2H_5	CH_3	CH_3	0.054	1 $CHCl_3$	1684
10	Benzyl methyl-2-chloroethylcarbamate	C_7H_7	CH_3	CH_2CH_2Cl	.11	1 $CHCl_3$	1691
11	N-Carbobenzyloxy-N-methyl-2-aminoethyl carbamate (II)	C_7H_7	CH_3	$CH_2CH_2OCONH_2$	.046	1 $CHCl_3$	1687, 1722
	Linear carbamates with cyclic nitrogen atom 		R_1–R_2				
12	N-Carboethoxy-1,3-oxazolidine (III)	C_2H_5	CH_2–OCH_2CH_2–		0.05	1 CCl_4	1706
13	N-Carboethoxy-2-pentamethyleno-1,3-oxazolidine	C_2H_5	C_5H_{10}–OCH_2CH_2–		.068	1 $CHCl_3$	1678
14	N-Carbopropoxy-2-pentamethyleno-1,3-oxazolidine	C_3H_7	C_5H_{10}–OCH_2CH_2–		.10	1 $CHCl_3$	1678
15	N-Carboethoxy-2-oxazolidone	C_2H_5	C(O)–OCH_2CH_2–		.05	1 $CHCl_3$	1722
16	N-Carbopropoxy-2-oxazolidone	C_3H_7	C(O)–OCH_2CH_2–		.042	1 $CHCl_3$	1718
17	N-Carboallyloxy-2-oxazolidone	C_3H_5	C(O)–OCH_2CH_2–		.050	1 $CHCl_3$	1718
18	N-Carbobenzyloxy-2-oxazolidone	C_7H_7	C(O)–OCH_2CH_2–		.073	1 $CHCl_3$	1726
19	N-Carbo-*p*-nitrobenzyloxy-2-oxazolidone	$C_7H_6NO_2$	C(O)–OCH_2CH_2–		.036	1 $CHCl_3$	1731
20	N-Carbobenzyloxy-*cis*-4,5-tetramethyleno-2-oxazolidone (IV)				.095	1 $CHCl_3$	1720
21	N-Carbobenzyloxy-*trans*-4,5-tetramethyleno-2-oxazolidone (V)	C_7H_7			.070	1 $CHCl_3$	1726

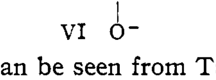
[a] Shows the amide C=O band at 1675 cm.$^{-1}$. [b] Shows the chlorocarboxy C=O band at 1768 cm.$^{-1}$.

Discussion

It can be seen from Table I that, as in the case of amides, the different classes of simple carbamates, primary, secondary and tertiary, may in fact be identified by their characteristic carbonyl frequency. Thus, a frequency of 1725 ± 3 cm.$^{-1}$ is common to all the primary carbamates reported here, a frequency of 1714 ± 9 cm.$^{-1}$ (1722–1705 cm.$^{-1}$) is typical for all the secondary carbamates and a value of 1687 ± 4 cm.$^{-1}$ represents the frequency of all the tertiary carbamates. The somewhat wide limits of the secondary carbamate frequency region are caused by having them include two secondary carbamates in which two special effects are operating to respectively increase and decrease the normal carbonyl frequency. If these cases are ignored, the limits can be set as 1714 ± 3 cm.$^{-1}$ but then only on the basis of two examples. In the case of the primary–secondary carbamate (no. 4) there appears only one carbonyl band as can be expected from the nearness of the characteristic ranges for the primary and secondary carbamic groups, which probably causes the merging together of the two carbonyl absorptions. The united carbonyl band would be expected to occur about half way between 1714 and 1725 cm.$^{-1}$, in good agreement with the observed value of 1718 cm.$^{-1}$. In the case of the primary–tertiary carbamate (no. 11) the interval between the corresponding regions is bigger, and the two absorptions appear therefore as two separate bands at 1687 and 1722 cm.$^{-1}$.

The value of 1728 cm.$^{-1}$ found here for the carbonyl group absorption of an oil paste of ethyl carbamate is in line with that obtained for an oil paste of the similar compound no. 3 (1726 cm.$^{-1}$) and agrees with the value of 1725 cm.$^{-1}$ obtained for it in solution as well as with the value of 1724 cm.$^{-1}$

of benzyl carbamate in solution. This value contradicts, however, the value of 1661 cm.$^{-1}$ given by Randall, *et al.*,[2] for the C=O frequency of an oil paste of ethyl carbamate (urethan), although their spectrum also shows a shoulder at 1730 cm.$^{-1}$, which after subtracting the atmospheric water vapor absorption in this region may turn out to be a strong band. It is true that an oil paste (but not a chloroform solution) of ethyl carbamate shows also strong and diffuse bands at about 1662 and 1614 cm.$^{-1}$, but none of these can be ascribed to the C=O frequency as can be judged from the values cited above for this frequency in similar compounds. Another argument against such an assignment is that in analogy to amides[4] one must assume the primary carbamate C=O group to absorb at a higher frequency than the C=O group of secondary and tertiary carbamates because of a stronger contribution from the resonating structure VI to the actual structure of the carbamates in the



$$R_1R_2N^+{=}\underset{\displaystyle O^-}{\underset{|}{C}}{-}OR_3$$

VI

latter case. It can be seen from Table I that this is the case if we assign, as was done above, the 1725 cm.$^{-1}$ band to the C=O stretching vibration of primary carbamates. If, however, the 1662 cm.$^{-1}$ band is assigned to this stretching vibration, then the primary carbamate C=O absorption is not higher than the secondary and tertiary carbamate C=O absorption at 1714 and 1687 cm.$^{-1}$, respectively, but lower. This 1662 cm.$^{-1}$ band also cannot be due to a strongly hydrogen bonded C=O frequency of the solid state since the C=O oil paste frequency of N-carboxyglycine dibenzyl ester (no. 5; see also no. 3) appearing at 1715 cm.$^{-1}$ is not materially different from the solution frequency while it is still mainly due to the carbamic group as can be judged from the fact that there is no other remarkable band down to 1530 cm.$^{-1}$. This means that in contradistinction to the amidic groups[4] the carbamic groups are not much affected by hydrogen bonding. This might be due to the lower polarization of its C=O double bond because of the electronegative effect of the neighboring OR group and has its analogy in ketones, the C=O frequency of which is also only slightly affected by ordinary hydrogen bonds.[5] The 1662 and 1614 cm.$^{-1}$ bands (Randall, *et al.*,[2] give 1661 and 1618 cm.$^{-1}$) seem therefore to stem from a splitting of the carbamic N–H group bending frequency because of the presence of two such hydrogen atoms here, the corresponding frequency in the case of solid primary amides[4] being shown at 1620–1650 cm.$^{-1}$. Such a splitting of a vibration because of a doubling of the vibrating unit on the same atom is very common.[6] In a chloroform solution these bands move to lower frequencies and unite in a broad band centered at about 1590 cm.$^{-1}$. This fact supports the above assignment, for the primary amide N–H band also behaves similarly by moving to about 1600 cm.$^{-1}$ in solution.[4] The Raman band observed for this substance in the melted form[7] at about 1692 cm.$^{-1}$ (besides a band at 1606 cm.$^{-1}$) may be a joint band made up of the bands at about 1728 and 1662 cm.$^{-1}$.

The value of 1714 ± 9 cm.$^{-1}$ found here for the C=O frequency in secondary carbamates agrees with the value of 1706 cm.$^{-1}$ given by Randall, *et al.*,[2] for ethyl N-methylcarbamate and with the value of 1704 cm.$^{-1}$ found by Baker and Joseph[8] in the case of an oil paste of a complex secondary carbamate which contains a hydroxy group in a γ-position to the carbonyl group. The somewhat lower carbonyl frequency in this case, relative to the usual frequency of about 1714 cm.$^{-1}$, as also in the case of compound 6, is probably the result of an internal hydrogen bond between the γ-hydroxy group and the carbonyl group (chelation). The small increase in the C=O frequency of I (no. 8) —1722 cm.$^{-1}$—seems to be due to the strong negative inductive effect of the chlorocarboxy group on the carbamic C=O group polarization. The even higher frequencies of this group observed by Randall, *et al.*,[2] in various substituted carbamates (*e.g.*, ethyl methoxycarbamate (methoxyurethan), 1727 cm.$^{-1}$; ethyl N-α-toluylcarbamate (phenacetylurethan), 1748 cm.$^{-1}$) must also be explained similarly, the effect of the substituents being here stronger because of their direct bond to the nitrogen atom. The frequencies of 1727 and 1745 cm.$^{-1}$ observed[3b] for the C=O group (in the undiluted phase) of ethyl N-trifluoromethylcarbamate and ethyl N-heptafluoropropylcarbamate, respectively, are probably fully analogous.

Thus it is clear that the C=O frequency of simple secondary carbamates appears at about 1715 cm.$^{-1}$ both in solution in chloroform and in the solid phase. This value contradicts the figures of 1735 and 7000 (probably a misprint for 1700) cm.$^{-1}$ reported by Thompson, *et al.*,[1b] for the C=O band in secondary urethans in chloroform solution and the liquid or solid phase, respectively (without giving any actual value). The values given by Thompson, *et al.*,[1b] for the C=O absorption of primary and tertiary urethans in chloroform solution are, however, in good agreement (1728 and 1690 cm.$^{-1}$, respectively) with the results reported above. Their value of 1690 cm.$^{-1}$ for undiluted primary urethans seems again to be due to nonresolution of the broad bands at about 1725 and 1660 cm.$^{-1}$.

The NH bending frequency appeared at 1530 cm.$^{-1}$ in an oil paste of compound 5 (Thompson, *et al.*,[1b] give 1540 cm.$^{-1}$ for a N–H bending in the solid or liquid phase of secondary urethans; see also ref. 3a) and at 1512 cm.$^{-1}$ in chloroform solution (Thompson, *et al.*, 1530). Compound 6 showed this band in carbon tetrachloride solution at 1516 cm.$^{-1}$, compound 7 showed a broad N–H bending absorption at 1514 cm.$^{-1}$ in $CHCl_3$ (both an amidic and a carbamic band) and compound 8 showed it (in $CHCl_3$) at 1509 cm.$^{-1}$. The corresponding amidic band appears[9] in solution at 1550–1510 cm.$^{-1}$ and in the solid phase at 1570–1515 cm.$^{-1}$.

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(5) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

(6) See, *e.g.*, E. D. Bergmann and S. Pinchas, *Rec. trav. chim.*, **71**, 161 (1952).

(7) J. Wagner, *Z. physik. Chem.*, **B43**, 333 (1939).

(8) B. R. Baker and J. P. Joseph, THIS JOURNAL, **77**, 15 (1955).

(9) Reference 1, p. 176.

The value of 1687 ± 4 cm.$^{-1}$ for the frequency of the tertiary carbamates means that while the first alkyl group introduced into the primary carbamate molecule decreases its frequency by about 10 cm.$^{-1}$ only, the second alkyl group decreases it by about 25 cm.$^{-1}$. The same phenomenon is also shown by amides in dilute solution as can be judged from the values of 1690 (primary), 1680 (secondary) and 1650 cm.$^{-1}$ (tertiary).[4] The reason for this behavior is difficult to see but may be connected with the direction of the positive inductive effect of the alkyl groups (which increases the contribution of the polar form VI to the actual structure of the carbamate molecule). Thus, because of the pyramidal form of the trivalent nitrogen atom[10] (with the lone pair of electrons above it), this effect is directed, in monoalkyl carbamates, not toward the N–CO bond but at an angle to it, while in dialkylcarbamates the resultant of the effects of the two alkyl groups is (taking in account its projection on the basal plane) in this direction and is therefore much more efficient in increasing the contribution of the resonating structure VI to the structure of the tertiary carbamates.

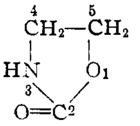
If the results for the linear carbamates which contain a cyclic nitrogen atom are examined, it can be seen that their C=O frequency reflects clearly the electronic effects of their substituents, especially those in the 2-position of the oxazolidine ring. Thus, N-carboethoxy-1,3-oxazolidine, which bears no substituent in this position, absorbs at 1706 cm.$^{-1}$ while its 2-pentamethylene derivative (as also the similar compound 14) absorbs at 1678 cm.$^{-1}$. This decrease in frequency is probably the result of the positive inductive effect of the 5 methylene groups, attached in the latter case to the 2-carbon atom, which strengthens the polarization of the carbonyl group. The reason for the value of 1706 cm.$^{-1}$ for N-carboethoxy-oxazolidine itself which is higher than that of ordinary tertiary carbamates (1687) seems to be its –CH$_2$O– group, attached to the nitrogen atom, which probably does not possess a positive inductive effect. This compound should therefore be looked at, in this respect, as a secondary, rather than tertiary, carbamate which absorbs in this region.

In the case of the N-carboalkoxy-2-oxazolidones, the substituent in the 2-position (the oxygen atom) has a strong negative inductive effect, and therefore an increase of their carbamate carbonyl frequency must be expected. Indeed, all the oxazolidonic carbamates measured (no. 15–21) show this band in the higher frequency range of 1718–1731 cm.$^{-1}$. This value may be compared with the value of 1736 cm.$^{-1}$ obtained by Randall, *et al.*,[2] for the carbamic C=O frequency of the somewhat similar ethyl methylbenzoylcarbamate. It is interesting to note that the highest frequency is observed with the *p*-nitrobenzyl ester where there exists an appreciable electron attraction away from the carbamic C=O group. This attraction would of course tend to increase the bond strength of this carbonyl group.

The 2-Oxazolidone C=O Absorption.—If the carbamic ester grouping is part of a five-membered ring, *e.g.* in 2-oxazolidones, then an additional factor must be taken into account when its C=O frequency is considered. This factor is the strain of such a five-membered ring which as a rule increases its exocyclic stretching frequencies.[11] This strain is apparent in the C=O frequency of γ-lactones which rises to about 1770 cm.$^{-1}$ as compared with the value of about 1740 cm.$^{-1}$ in the case of esters and six-membered lactones.[12] The C=O frequency of oxazolones is also very high,[13] at about 1820 cm.$^{-1}$, partly because of this strain. Thus the C=O frequency of simple 2-oxazolidones would already be expected to be quite high, while in N-acetylated oxazolidones this frequency would be expected to rise even more. Table II shows that this is really the case.

Table II

The Frequency of the 2-Oxazolidone C=O Stretching Vibration



Material	Concn. g. + 1 ml. CHCl$_3$[a]	Frequency, cm.$^{-1}$	Bands in 1100–1000 cm.$^{-1}$ region
2-Oxazolidone	0.056	1760(broad)	1085, 1029
4-Dimethyl-	.034	1748	1043
N-Methyl-	.05	1746	1049
N-Phenyl-	.031	1753	1053
N-Acetyl-	.056	1785[b]	1057, 1038
N-Benzoyl-	.050	1793[c]	1100, 1041
N-Carboethoxy-	.050	1798	1079, 1043
N-Carbopropoxy-	.042	1795	Not measured
N-Carboallyloxy-	.050	1805	Not measured
N-Carbobenzyloxy-	.073	1810	1085, 1039
N-Carbo-*p*-nitro benzyloxy-	.036	1798	Not measured
4,5-Tetramethyleno-2-oxazolidones			
N-Benzoyl-	0.048[e]	1791[d]	1099, 1059
N-Carbobenzyloxy-*cis*- (IV)	.095	1807	1073, 1033
N-Carbobenzyloxy-*trans*- (V)	.070	1807	1090, 1037

[a] Unless otherwise stated. [b] The amidic CO group absorbs at 1695 cm.$^{-1}$. [c] The amidic CO group absorbs at 1679 cm.$^{-1}$. [d] The amidic CO group absorbs at 1677 cm.$^{-1}$. [e] 1 ml. CCl$_4$.

It is interesting to note that N-methyloxazolidone absorbs at a lower frequency than oxazolidone (1746 as compared with 1760 cm.$^{-1}$) as can be expected from the inductive effect of the N-methyl group. The high polarization of N-methyloxazolidone, as evidenced by its high electric moment,[14] would also suggest that its CO frequency is not relatively high. This decrease in frequency is especially remarkable because of the stable hydrogen bonded dimer form of 2-oxazolidone (VII) which persists even in dilute solution,[14] since such a structure would probably diminish considerably the

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(10) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," new ed., Oxford University Press, Oxford, 1942, p. 39.

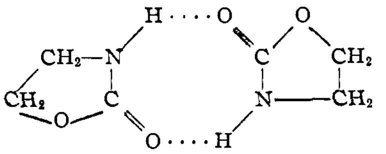
(11) P. Bladon, J. M. Fabian, H. B. Henbest, H. B. Koch and G. W. Wood, *J. Chem. Soc.*, 2410 (1951).

(12) J. F. Grove and H. A. Willis, *ibid.*, 877 (1951).

(13) H. W. Thompson, R. R. Brattain, H. M. Randall and R. S. Rasmussen, "The Chemistry of Penicillin," Princeton Univ. Press, Princeton, N. J., 1949, p. 400.

(14) E. Fischer, *J. Chem. Soc.*, 4525 (1952).

C=O frequency of oxazolidone from its "free" value. It must be added that when methyl oxazolidone was measured in a carbon tetrachloride solution and not in chloroform (which is known to decrease the C=O frequency of the materials dissolved in it[15]), it showed this band at about 1760 cm.$^{-1}$.


VII

The value of 1724 cm.$^{-1}$ is reported in the literature[16] for the CO frequency of 2-oxazolidone in the solid phase.

The case of 4-dimethyloxazolidone seems to be similar and here also a stable dimer must be expected with an accompanying decrease in the C=O frequency. The further decrease of this frequency in this case (1748 as compared with 1760 cm.$^{-1}$ for oxazolidone) probably is due to the positive inductive effect of the two neighboring methyl groups on the nitrogen atom, in analogy to the effect of the pentamethylene group in the case of carbamates 13 and 14 (see above).

The relatively low C=O frequency of N-phenyloxazolidone (1753 cm.$^{-1}$) is also remarkable, especially since in anilides the phenyl ring has an opposite effect.[1a] In N-phenyl carbamates, however, the C=O frequency observed in the solid phase was also relatively low (1690–1720 cm.$^{-1}$).[3a]

In comparison with the oxazolidonic C=O frequency, that of 2-pyrrolidone and N-methyl-2-pyrrolidone was also measured. Pyrrolidone showed the CO band in carbon tetrachloride solution (0.046 g. + 1 ml.) at 1678 cm.$^{-1}$ and N-methylpyrrolidone, in chloroform, at 1688 cm.$^{-1}$. 2-Pyrrolidone is known to form hydrogen bonded dimers even in dilute solutions[17] and its lower frequency is therefore understandable. Mecke and Mecke[16] give the value of 1690 cm.$^{-1}$ for this frequency in the liquid phase and 1706 cm.$^{-1}$ for a 0.05–0.1 mole per liter solution in CCl_4. The last value seems to be due to the "free" molecule which is probably present in this dilution. The much lower frequency of N-methylpyrrolidone, relative to that of N-methyloxazolidone (1746 cm.$^{-1}$), seems to suggest a much larger ionic character in the former case as is the case in amides in general. This assumption, however, is at variance with the present view[14,18] based on electric moment measurements. It must also be pointed out that in going over from an open structure to a five-membered ring the tertiary carbamates suffer the biggest increase in the CO frequency. Thus the increase in this case is about 60 cm.$^{-1}$ as compared with about 45 cm.$^{-1}$ for secondary carbamates, 40 cm.$^{-1}$ for tertiary amides and 30 cm.$^{-1}$ for saturated esters.

The acyl groups can again be observed, in Table II, to increase appreciably the C=O frequency, this effect being highest in the case of the aromatic acyl derivatives (*e.g.*, N-benzoyl-oxazolidone, 33 cm.$^{-1}$), maybe because of the higher polarization of the acylic C=O group in this case. The still higher oxazolidonic C=O range (1795–1810 cm.$^{-1}$) of the N-carboalkoxy-oxazolidones is to be expected in the light of the increased electron attraction power of the carboalkoxy group.

Apart from the oxazolidone C=O frequency another band seems to be characteristic for the oxazolidonic ring. This medium-strong band appears at 1029–1059 cm.$^{-1}$ in all the measured compounds containing such a ring, as can be seen from Table II. Sometimes this band is split into two branches. These bands seem to be due to the C–OC(O) ring stretching vibrations in analogy to the antisymmetrical ring stretching band of tetrahydrofuran[19] at about 1080 cm.$^{-1}$ and to the N–C–O stretching bands at about 1160, 1130 and 1100 cm.$^{-1}$ of oxazolidines.[20] The Raman band found in solid primary carbamates[7] at about 1120 cm.$^{-1}$ may be the counterpart of this band in the case of the open NC(O)O–C group. The decrease in the stretching frequency of the C–OR bond when this is part of a strained ring is then the usual behavior of such (endocyclic) bonds.[11]

Experimental

The infrared absorption measurements were carried out with a Perkin–Elmer, model 12C, infrared spectrometer equipped with a sodium chloride prism. The synthesis of most of the materials used in this investigation has already been described by Ben-Ishai.[21] The rest of them were either of commercial origin or synthesized according to the literature.

Ethyl carbamate, showed (in solution) also bands at: 3370, 1589, 1468, 1403, 1373, 1324, 1237, 1170, 1061, 985, 956, 889 and 849 cm.

2-Aminoethyl carbamate hydrobromide showed (in an oil paste) the NH_3^+ bands at 1970 and 1920 cm.$^{-1}$ (besides a band at about 3200 cm.$^{-1}$.

2-(Carboethoxyamino)-ethanol showed (in CCl_4 solution) also bands at 3360, 2930, 1516, 1379, 1330, 1248, 1081 and 1036 cm.$^{-1}$.

Carbobenzyloxyglycine-(2-chloroethyl)-amide showed also bands (in $CHCl_3$) at 1514, 1452, 1355, 1261, 1049 and 981 cm.$^{-1}$.

N-Carboethoxy-2-pentamethyleno-1,3-oxazolidine showed (in $CHCl_3$) also bands at 1425, 1379, 1349, 1330, 1277, 1175, 1139, 1073, 1037, 973, 946, 910 and 844 cm.$^{-1}$.

N-Carbopropoxy-2-pentamethyleno-1,3-oxazolidine showed (in $CHCl_3$) also bands at 1452, 1419, 1363, 1341, 1324, 1280, 1237, 1132, 1072, 1024, 978, 942, 910 and 843 cm.$^{-1}$.

N-Carboethoxy-2-oxazolidone showed (in $CHCl_3$) also bands at 1477, 1385, 1307, 1184, 1079 and 1043 cm.$^{-1}$.

N-Carbobenzyloxy-2-oxazolidone showed (in $CHCl_3$) also bands at 3475, 2925, 1590, 1462, 1386, 1315, 1085, 1039, 981 and 908 cm.$^{-1}$.

2-Oxazolidone showed (in $CHCl_3$) bands also at 3440, 3290, 3160, 2925, 1484, 1399, 1332, 1320, 1246, 1085, 1029, 960 and 924 cm.$^{-1}$.

4-Dimethyl-2-oxazolidone showed (in $CHCl_3$) bands also at 3440, 3240, 1466, 1377, 1294, 1235, 1043, 986 and 937 cm.$^{-1}$.

N-Phenyloxazolidone showed (in $CHCl_3$) bands also at 2930, 1599, 1487, 1406, 1309, 1130, 1053, 991, 955 and 899 cm.$^{-1}$.

N-Acetyloxazolidone showed also (in $CHCl_3$) bands at 3465, 3160, 2925, 1482, 1383, 1315, 1240, 1146, 1057, 1038 and 956 cm.$^{-1}$.

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[15] See, *e.g.*, K. Dobriner, E. R. Katzenellenbogen and R. N. Jones, "Infrared Absorption Spectra of Steroids," Interscience Publishers, Inc., New York, N. Y., 1953, p. ix.

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N-Benzoyloxazolidone showed also (in $CHCl_3$) bands at 3160, 2925, 1602, 1481, 1450, 1379, 1328, 1186, 1100, 1041, 987, 912 and 882 cm.$^{-1}$.

N-Benzoyl-4,5-tetramethyleno-2-oxazolidone showed also (in CCl_4) bands at 2925, 1596, 1454, 1355, 1330, 1309, 1253, 1205, 1177, 1126, 1099, 1059, 999, 969, 942, 907 and 896 cm.$^{-1}$.

2-Pyrrolidone and **N-methyl-2-pyrrolidone** were commercial products purified by vacuum distillation.

REHOVOTH, ISRAEL

[CONTRIBUTION OF THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

Polar Factors in Radical Dissociations. Kinetics of Decomposition of *meta*-Substituted Phenylazotriphenylmethanes[1a]

BY STANLEY SOLOMON, CHI HUA WANG AND SAUL G. COHEN[1b]

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meta-Substituted phenylazotriphenylmethanes, $m\text{-X—}C_6H_4N{=}NC(C_6H_5)_3$, X = CH_3, Br, NO_2, (H), have been prepared and decomposed in toluene at two temperatures. The decompositions showed first-order kinetics with activation energies in the range 26–30 kcal. mole^{-1}. The substituent CH_3 led to increased rates, the substituents Br and NO_2 to decreased rates of decomposition, the effects being quite similar to those of *p*-substituents studied previously. The results for *m*-substituents were correlated by the Hammett equation, ρ −0.85, and indicated that phenyl radicals may be rendered less stable by electron withdrawal. Factors affecting homolytic dissociation processes are discussed. Decomposition of phenylazotriphenylmethane in acetic acid led to benzene (>40% yield), to biphenyl (10% yield) and to no succinic acid. The origin of the products is discussed.

As part of our study of the effects of structure on the homolytic dissociation of organic compounds, which lead to the formation of free radicals, we have been examining the effects of substituents in the phenyl group of phenylazotriphenylmethanes on the kinetics of their decomposition. The ease with which homolytic dissociation occurs, or the strength of the bond or bonds concerned may be considered in terms of steric effects, polar factors, and the difference in the resonance stabilization of the ground states and transition states.

The decomposition of substituted ethanes[2] R_3–C–C–R_3 shows marked increase in rates and decrease in activation energies as the alkyl groups R are made more complex or are changed to aryl groups, the variations resulting from steric factors, which affect the central carbon–carbon bond, and resonance stabilization of the radicals. Azo-bis-alkanes and azo-bis-arylalkanes $R_3C{—}N{=}N{—}CR_3$ are related materials, in which the azo linkage facilitates decomposition while reducing steric effects. Substitution of α-alkyl and aryl groups for hydrogen in the parent compound azomethane, R = H, leads to successive and approximately additive increase in rate and decrease in activation energy, which have been interpreted in terms of resonance stabilization of the radicals,[3] and hence of the transition states. Steric effects have also been observed in the decomposition of certain azo compounds, largely due to β-substituents.[4]

Substituents in the nuclei of hexaarylethanes, whether electron attracting or electron donating, increase the extent of their dissociation, the large effects of *o*-substituents commonly being attributed to steric and resonance factors, and the effects of *p*-substituents, to resonance.[5] The effect of *m*-substituents, often attributed to steric factors, may result largely from the charge (+ or −) which they impose upon the aromatic rings to which they are attached, leading, in symmetrically substituted ethanes, to electrostatic repulsions between the two halves and weakening of the central bond. That the effect of *m*-substituents is comparable to and frequently greater than that of *p*-substituents indicates that this polar factor may be of importance in the latter case also.

In the decomposition of substituted benzoyl peroxides,[6] electron-donating substituents were found to increase the rates, electron-attracting substituents, (except nitro) to decrease them, and the data fitted the Hammett equation fairly well, ρ −0.38. This was interpreted[6a] in terms of the effects of the substituents on the size of the negative ends of the dipoles, postulated to exist at the central oxygen–oxygen bond and thus on repulsive forces operating between the two halves of the molecules. Similar effects of substituents were observed in the decomposition of *t*-butyl perbenzoates.[7] Also, in the dissociation of five symmetrically substituted 1,1,4,4-tetraphenyl-2,3-dibenzoyltetrazanes,[8] in which the phenyl substituents were CH_3, H and Br, the equilibrium constants were correlated with the Hammett equation, ρ −1.52. This was interpreted as resulting from stabilization by electron-donating substituents of the positive charge on the α-nitrogen in one of the resonance forms of the hydrazyl radicals. Further study of the dissociation of these tetrazanes indicated that the Hammett equation success-

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[1] (a) Taken in part from a dissertation submitted by Stanley Solomon in partial fulfillment of the requirements for the M.A. degree in Chemistry, Brandeis University. (b) To whom inquiries should be addressed.

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