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THE KINETICS OF QUATERNIZATION OF N,N,N′,N′-TETRAMETHYL-α,ω-ALKANEDIAMINES WITH BUTYL BROMIDE

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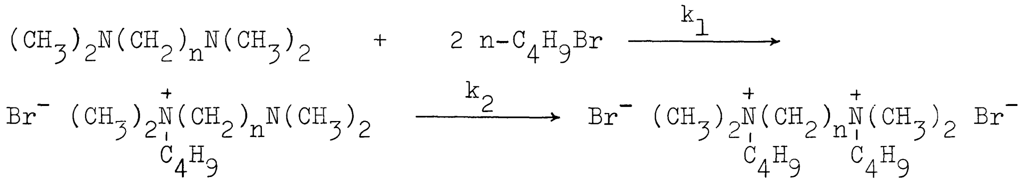
Competitive and consecutive reaction of N,N,N′,N′-tetramethyl-α,ω-alkanediamines with butyl bromide was studied in propylene carbonate at different temperatures. The kinetic data have revealed the effects of the chain lengths of alkanediamines on the reaction.

The kinetics of quaternization using ditertiary amines or dihalides is considered to be important as an approach for the elucidation of formation of ionene polymers. In the previous report1) the correlation between the reactivity and the chain length of dibromoalkanes in the reaction with tertiary amines was discussed.



$$(CH_3)_2N(CH_2)_nN(CH_3)_2 \quad + \quad 2\ n\text{-}C_4H_9Br \xrightarrow{k_1}$$
$$Br^-\ (CH_3)_2\underset{C_4H_9}{\overset{+}{N}}(CH_2)_nN(CH_3)_2 \xrightarrow{k_2} Br^-\ (CH_3)_2\underset{C_4H_9}{\overset{+}{N}}(CH_2)_n\underset{C_4H_9}{\overset{+}{N}}(CH_3)_2\ Br^-$$

In the present paper the kinetic data on the reaction of ditertiary amines with butyl bromide are reported. Similarly to the reaction of ethylene dibromide (EDB) described in the previous report N,N,N′,N′-tetramethyl-1,2-ethanediamine(TED) showed fairly smaller reactivity in the 2nd step of the reaction than in the 1st step and this fact was compatible with the results of research on the formation of ionene polymers carried out by Rembaum and his coworkers2,3) that only monomeric or cyclic products were generally formed from EDB and TED.

TED was redistilled and the other tertiary diamines were prepared by methylating corresponding primary diamines according to the Eschweiler-Clark method. The kinetic determination was carried out according to the procedure described before1) and the rate constants were calculated by the Frost-Schwemer method using Burkhard's table.4) As the ratio , $1/\kappa = k_1/k_2$, for TED was too large to apply the Frost-Schwemer method, so k_1 was obtained from the usual second order rate equation for the conversion of less than 50% of amino group and k_2 was calculated from the slope of plot for the conversion of more than 50% vs. the time of reaction.

As shown in Table 1, the values of $1/\kappa$ varied with n values in the following order: $n = 2 \gg 3 > 4 > 6 \approx 10$. The reactivity of diamines is greatly affected by their chain lengths in the lower diamines. Such tendency in $1/\kappa$ values owes largely to k_2 values, because the variation in k_2 values with increase of n value is far larger than in k_1. Also in the reaction of EDB with tertiary amines reported before1)

Table 1. Quaternization of N,N,N',N'-tetramethyl-α,ω-diaminoalkanes with butyl bromide in propylene carbonate

$(CH_3)_2N(CH_2)_n$-$N(CH_3)_2$	Reaction step	10^3 k ($l.mol.^{-1}sec.^{-1}$)						E	$-\Delta S^{\ddagger}$
		50°C	1/κ	63°C	1/κ	75°C	1/κ	($kcal.mol.^{-1}$)	(e.u.)
n= 2	1	1.91	109	4.05	133	7.14	147	11.8	36.6
	2	0.0175		0.0304		0.0486		9.13	54.2
3	1	2.42	18.1	5.28	19.8	9.33	21.0	12.1	35.2
	2	0.134		0.267		0.444		10.7	45.2
4	1	2.49	5.61	5.35	5.73	9.65	5.94	12.1	35.1
	2	0.444		0.933		1.63		11.6	40.0
6	1	2.43	2.97	5.17	2.97	9.87	2.90	12.5	33.9
	2	0.817		1.74		3.40		12.7	35.4
10	1			4.61	2.85	9.39	2.82	13.6	30.7
	2			1.62		3.30		13.8	32.8

1/κ has shown very large value similar to the result in the present reaction. The above results suggest that it may be difficult to form polymer from TED and EDB, as was pointed out by Rembaum et al.

Activation parameters, E and $\Delta S^{\ddagger}$, for the 1st step show little variations depending on n values of the diamines, but for the 2nd step both parameters are much smaller when n is 2 or 3 than when n is large. The differences, E_1-E_2 and $\Delta S_1^{\ddagger} - \Delta S_2^{\ddagger}$, show the similar tendency to 1/κ values with incerase of n value. In case of n=6 and 10 these differences are very small and 1/κ values are nearly equal. From the above results it may be supposed that in case of n=6 or 10 there are little effects of the 1st quaternized amino group on the 2nd quaternization. However, 1/κ values are larger than unity even for these diamines(n=6 and 10) and this fact seems to be largely caused by the statistical factor with the concentration of reactive amino group, as in case of the dissociation of alkanediamines.[5)]

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