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Contribution of Ring Strain and Basicity to Reactivity of Cyclic Ethers in Cationic Copolymerization

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Summary

Relative reactivity of cyclic ethers, including epoxide, oxetane, tetrahydrofuran, and tetrahydropyran, was evaluated with their basicity and free energy of polymerization. The logarithm of relative reactivity, $1/r_n$, of m-membered ring ethers with i substituents to n-membered ring monomers with j substituents can be expressed by a linear combination of the differences in basicity, $\Delta(pK_b)_{m\cdot i-n\cdot j}$, and in free energy, $\Delta(\Delta G)_{m\cdot i-n\cdot j}$:

$$\log(1/r_n) = \alpha\,\Delta(\Delta G)_{m\cdot i-n\cdot j} + \beta\,\Delta(pK_b)_{m\cdot i-n\cdot j} + \gamma$$

where, α, β, and γ are constants. The changes in basicity and free energy of these compounds can be obtained as

$$\Delta(pK_b)_{m\cdot i-n\cdot j} = b_m \sum_i \sigma^* - b_n \sum_j \sigma^* + \Delta(pK_b)_{(m-n)\cdot 2(\mathrm{CH_3})}$$

$$\Delta(\Delta G)_{m\cdot i-n\cdot j} = a_m \sum_i \sigma^* - a_n \sum_j \sigma^* + \Delta(\Delta G)_{(m-n)\cdot 2(\mathrm{CH_3})}$$

Here a_k and b_k ($k = m, n$) are constants, σ^* is the polar substituent constant by Taft, and $\Delta(X)_{(m-n)\cdot 2(\mathrm{CH_3})}$ ($X = \Delta G$, pK_b) are the differences in basicity and free energy between dimethyl-substituted compounds of m- and n-membered rings, respectively.

The ring-opening polymerizability of saturated heterocyclic compounds was discussed in the light of the heat, entropy, and free-energy changes for hypothetical polymerizations of liquid monomers to condensed polymers (*1*). Recently, several workers have studied the cationic copolymerization of cyclic ethers, formals, and esters, and now a large number of copolymerization parameters are available. However, there is a little quantitative study on the reactivity of these compounds.

Iwatsuki et al. (*2*,*3*) and also Sakai et al. (*4*) proposed that the correlation of the relative reactivity of the cyclic compounds in the cationic copolymerization with their basicity. Yamashita et al. (*5*) indicated that the basicity of the monomers is a factor in the cationic copolymerization of cyclic ethers, and concluded that the scatter observed in the relationship between pK_b and the relative reactivity of the monomers can be related to the ring strain or the free energy of polymerization. Aoki et al. (*6*) discussed the contribution of the ring strain of cyclic ethers to their relative reactivity.

These studies prompt us to report our quantitative treatment for the contributions of the basicity and the strain in the ring of cyclic ethers to their copolymerization reactivity.

RING STRAIN

A linear relationship can be observed between Taft's polar substituent constant, σ^*, and the free energy of polymerization of the cycloparaffins calculated by Dainton et al. (*7*). The best straight line has been found by the least-squares method (*9*) and shown by

$$(\Delta G)_{m\cdot i} = a_m \sum_i \sigma^* + (G)_{m\cdot 2(\mathrm{CH_3})} \qquad (1)$$

where $(\Delta G)_{m\cdot i}$ and $(\Delta G)_{m\cdot 2(\mathrm{CH_3})}$ are free energies of polymerization of *i*- and 1,1-dimethyl–substituted *m*-membered ring compounds,

TABLE 1

Correlation of Free Energy of Polymerization with σ^* for Cycloparaffines, $(\mathrm{CH_2})_{m-1}\mathrm{CR_2}$: $(\Delta G)_{m\cdot i} = a_m \sum_i \sigma^* + (\Delta G)_{m\cdot 2(\mathrm{CH_3})}$

Ring m	Constants in relationship a_m	$(\Delta G)_{m\cdot 2(\mathrm{CH_3})}$	Correlation coefficient[a]	No. of data used[b]
3	−8.59	−13.75	0.998	3
4	−7.71	−13.95	0.999	3
5	−7.16	4.88	0.994	3
6	−6.55	8.11	0.984	3

[a] See Ref. 9.

[b] ΔG°_{1c} in Table 3 of Ref. 7.

and a_m is constant and collected in Table 1. The σ^* values used in these calculations have been taken from Taft's review (*8*). This linearity can naturally be concluded from Dainton et al.'s assumption (*7*) in which steric repulsion effects of substituents were neglected in the calculation of the free energy of polymerization.

In this approach, the free energy of polymerization of cyclic ethers was assumed to be comparable to that of cycloalkanes (*1*) and to be expressed by Eq. (1). Therefore, the relative ring strain or the difference in the free energy of polymerization between i-substituted m-membered ring ethers and j-substituted n-membered ring monomers can be calculated by

$$\Delta(\Delta G)_{m\cdot i-n\cdot j} = a_m \sum_i \sigma^* - a_n \sum_j \sigma^* + \Delta(\Delta G)_{(m-n)\cdot 2(\mathrm{CH_3})} \qquad (2)$$

where a_k ($k = m$ and n) are constants and $\Delta(\Delta G)_{(m-n)\cdot 2(\mathrm{CH_3})}$ is the difference in the free-energy changes between dimethyl-substituted compounds of m- and n-membered rings, respectively.

$$\Delta(\Delta G)_{(m-n)\cdot 2(\mathrm{CH_3})} = (\Delta G)_{m\cdot 2(\mathrm{CH_3})} - (\Delta G)_{n\cdot 2(\mathrm{CH_3})} \qquad (3)$$

BASICITY

The role of ethers as hydrogen-bond acceptors has been investigated in a number of ways (*10,11*). Among the saturated cyclic ethers good agreement is found for the order of basicity regardless of the coordinating acid (*12*). At present we have inadequate information on the substituent parameters that might apply to cyclic systems but would expect that a series of cyclic ethers belonging to

TABLE 2

Correlation of Basicity with σ^* for Cyclic Ethers, $(\mathrm{CH_2})_{m-1}\mathrm{OCR_2}$: $(pK_b)_{m\cdot i} = b_m \sum_i \sigma^* + (pK_b)_{m\cdot 2(\mathrm{CH_3})}$

Ring	Constants in relationship		Correlation	No. of data
m	b_m	$(pK_b)_{m\cdot 2(\mathrm{CH_3})}$	coefficient[a]	used[b]
3	1.82	6.13	0.969	3
4	2.22	0.971	—	2
5	0.792	4.20	—	2

[a] See Ref. 9.
[b] See data of Table 3.

the same ring member should follow a rather good Taft plot. In fact, a linear relationship can be observed between σ^* and the basicity of ethers. The best straight line has been found by the least-squares method (9) and shown by

$$(pK_b)_{m \cdot i} = b_m \sum_i \sigma^* + (pK_b)_{m \cdot 2(CH_3)} \tag{4}$$

where $(pK_b)_{m \cdot i}$ and $(pK_b)_{m \cdot 2(CH_3)}$ are basicities of i- and 1,1-dimethyl-substituted m-membered ring ethers and b_m is constant and collected in Table 2.

The relative basicity between i-substituted m-membered ring ethers and j-substituted n-membered ring ones can also be expressed as

$$\Delta(pK_b)_{m \cdot i - n \cdot j} = b_m \sum_i \sigma^* - b_n \sum_j \sigma^* + \Delta(pK_b)_{(m-n) \cdot 2(CH_3)} \tag{5}$$

where b_k ($k = m$ and n) are constants and $\Delta(pK_b)_{(m-n) \cdot 2(CH_3)}$ is the difference in the basicity between 1,1-dimethyl–substituted ethers of m- and n-membered rings and can be calculated as

$$\Delta(pK_b)_{(m-n) \cdot 2(CH_3)} = (pK_b)_{m \cdot 2(CH_3)} - (pK_b)_{n \cdot 2(CH_3)} \tag{6}$$

Some unknown basicities of various cyclic ethers are estimated by Eq. (4) and collected in Table 3. The basicity of these ethers should be affected, as in the case of the free energy of polymerization, by the ring size and substituents. Thus it may be expressed by two factors, in which the first term is dependent on the ring members and the second depends on the substituents, whose steric effects are ignored in this approach.

RELATIVE REACTIVITY IN CATIONIC COPOLYMERIZATION

The propagation reaction in the cationic polymerization of heterocyclic compounds has been somewhat obscure. The trialkyloxonium ion (ion pair or free ion) is believed to be more stable than the carbonium ion derived by the ring opening of the oxonium ion, except for the resonance-stabilized carbonium ion. An S_N1 type of opening of the oxonium ion and in S_N2 attack of monomers to the oxonium ion are suggested to be the rate-determining step in the cationic polymerization of ethylene oxide, (*13*) and oxetane and tetrahydrofuran (*7,14–18*) respectively, while a carbonium ion is assumed to be the propagating species for cyclic formals (*19–23*).

If the propagation reaction proceeds as

$$\sim\!\sim C_n^+ + OM_n \overset{K_{nn}}{\rightleftarrows} \sim\!\sim C_n^+\text{—}OM_n \xrightarrow{k_{nn}} \sim\!\sim C_n^+ \tag{7}$$

$$\sim\!\sim C_n^+ + OM_m \overset{K_{nm}}{\rightleftarrows} \sim\!\sim C_n^+\text{—}OM_m \xrightarrow{k_{nm}} \sim\!\sim C_m^+ \tag{8}$$

the copolymerization equation reduces to the ordinary Mayo-Lewis equation

$$\frac{d(M_n)}{d(M_m)} = \frac{(M_n)}{(M_m)} \frac{r_n(M_n) + (M_m)}{(M_n) + r_m(M_m)} \tag{9}$$

where

$$\sim\!\sim C_k^+,\ \sim\!\sim C_k^+\text{—}OM_k,\ OM_k, \text{ and } (M_k)\ (k = m \text{ and } n)$$

are growing carbonium ion, oxonium ion, monomer and the concentration of monomer of k-membered ring, and K_{ll} and k_{ll} ($l = m$ and n) are the equilibrium and rate constants, respectively. Here r_k ($k = m$ and n) are expressed as

$$r_n = k_{nn}K_{nn}/k_{nm}K_{nm} \tag{10a}$$

$$r_m = k_{mm}K_{mm}/k_{mn}K_{mn} \tag{10b}$$

The monomer reactivity ratio should therefore include k and K. K should be proportional to the basicity, while k is the rate constant of an S_N1 type of opening of the derived oxonium ion. Thus we may explain the upperward deviation (*5*) of three-membered ethers and the downward deviation (*5*) of five- or six-membered ones in the relationship between log $1/r_1$ and pK_b for monomer M_2 by Eq. (10). The logarithm of relative reactivity, $1/r_n$, of i-substituted m-membered ring ethers to j-substituted n-membered ring ones, therefore, should be expressed by a linear combination of the differences in basicity, $\Delta(pK_b)_{m\cdot i-n\cdot j}$, and in free-energy change, $\Delta(\Delta G)_{m\cdot i-n\cdot j}$, as shown by

$$\log(1/r_n) = \alpha\ \Delta(\Delta G)_{m\cdot i-n\cdot j} + \beta\ \Delta(pK_b)_{m\cdot i-n\cdot j} + \gamma \tag{11}$$

where α and β are the empirical parameters to express the contribution of the ring strain and the basicity to the reactivity and γ is a correction term determined by M_n used as standard.

We picked up the data (*6,24–27*) on the cationic copolymerization of 3,3-bis-chloromethyloxetane with other cyclic ethers from Table 1 in Ref. 5 and show them in Table 3 together with calcu-

TABLE 3

Relative Reactivity in $BF_3 \cdot Et_2O$–Catalyzed Copolymerization of 3,3-Bis-chloromethyloxetane (M_1) with Cyclic Ethers (M_2), $O(CH_2)_{m-1}CR_1R_2$, at 0°C in CH_2Cl_2, and Their Basicity and Free-Energy Change

											$1/r_1$		
		Substituent			$(\Delta G)_{m \cdot i}$		$(pK_k)_{m \cdot i}$		r_1			Calcd.[f]	
No.	Ring m	R_1	R_2	$\Sigma\sigma^{*}$[a]	Calcd.[b]	Lit.[c]	Calcd.[d]	Obsvd.[e]	Obsvd.	Lit.	Obsvd.	A	B
1	4	H	H	0.980	−21.50	−21.5	3.15	3.13	—	—	—	—	—
2	4	CH_2Cl	CH_2Cl	2.10	−30.14	—	5.63	5.65	—	—	—	—	—
3	3	H	C_2H_5	0.390	−17.10	—	6.84	—	0.3	6	3.33	6.26	2.48
4	3	H	CH_3	0.490	−17.96	−18.1	7.02	6.94	0.3	24	3.33	5.27	2.39
5	3	H	$C_6H_5CH_2$	0.705	−19.80	—	7.70	—	0.45	6	2.22	1.01	1.52
6	3	H	H	0.980	−22.17	−22.1	7.91	—	0.5	24	2.00	2.17	1.96
7	3	H	CH_3OCH_2	1.01	−22.42	—	7.97	—	0.7	6	1.45	1.99	1.92
8	3	H	C_6H_5	1.09	−23.10	—	8.11	8.30	0.8	24	1.25	1.76	1.87
9	3	H	$C_6H_5OCH_2$	1.34	−25.26	—	8.57	—	1.1	6	0.91	1.10	1.69
10	3	H	CH_2Cl	1.54	−26.97	—	8.94	8.84	2–3	24	0.33–0.50	1.36	1.54
11[g]	5	H	CH_3	0.490	1.37	1.5	4.59	4.56	1.29	25	0.77		0.73
									2.7	27	0.37		
12[h]	5	H	H	0.980	− 2.14	− 2.2	4.98	5.00	0.82	26	1.22		0.97
13[g]	6	H	H	0.980	1.69	1.4	—	5.42	1.66	25	0.604		0.24

[a] See Ref. 8.

[b] By Eq. (1).

[c] See Ref. 7.

[d] By Eq. (4).

[e] Data in Ref. 5.

[f] By Eq. (11). See Table 4.

[g] Copolymerization in bulk.

[h] Copolymerization in toluene.

TABLE 4

Constants in Relationship
$\log(1/r_n) = \alpha\ \Delta(\Delta G)_{m\cdot i-n\cdot j} + \beta\ \Delta(pK_b)_{m\cdot i-n\cdot j} + \gamma$

Ethers	Constants in relationship			Correlation coefficient[a]	No. of data used[b]
	α	β	γ		
A 3-membered	−0.308	−1.89	7.10	0.980	8
B 3-, 5-, and 6-membered	−0.0949	−0.544	2.29	0.962	12

[a] See Ref. 9.
[b] See Table 3.

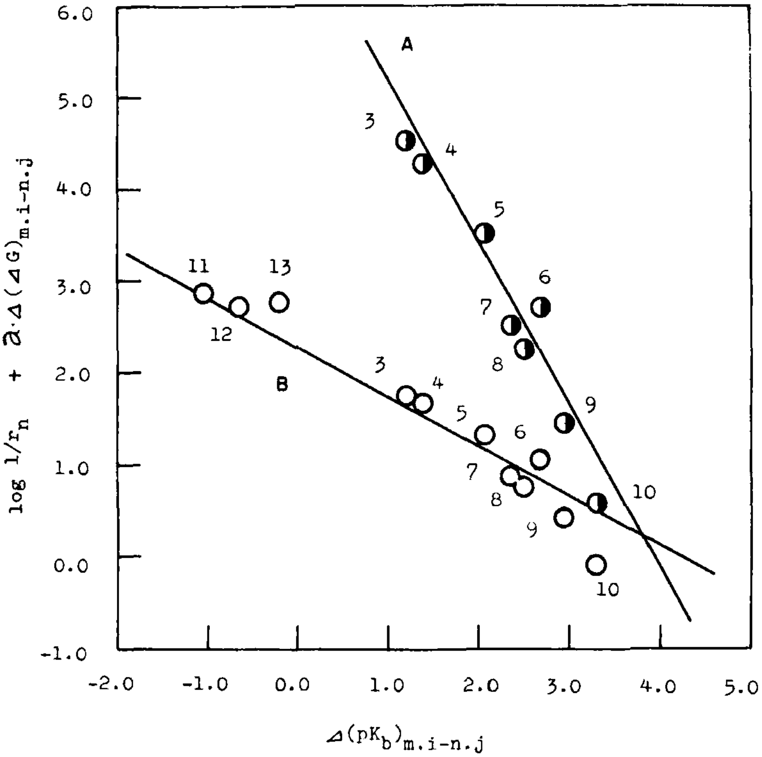

FIG. 1. Relationship between $\log(1/r_n) + \alpha\ \Delta(\Delta G)_{m\cdot i-n\cdot j}$ and $\Delta(pK_b)_{m\cdot i-n\cdot j}$ for $BF_3 \cdot Et_2O$-catalyzed copolymerization of 3,3-bischloromethyloxetane with cyclic ethers at 0°C in CH_2Cl_2. ◑, three-membered ring (A); ○, three-, five-, and six-membered ring (B). See Table 4.

lated and observed values of the basicity $(pK_b)_{m\cdot i}$, free-energy change $(\Delta G)_{m\cdot i}$, and $\Sigma\sigma^*$ values. The concepts of regression were applied to this case where the expected value of the random variable $\log(1/r_n)$ depends linearly on known quantities of differences in the free-energy change and the pK_b value. Maximum likelihood estimates of α, β, and γ were obtained by the method of least squares (9) and these values are shown in Table 4. As shown in Fig. 1, good correlations were observed between the relative reactivity corrected with $\Delta(\Delta G)_{m\cdot i-n\cdot j}$ and the $\Delta(pK_b)_{m\cdot i-n\cdot j}$ value. Therefore, the copolymerization parameter, $1/r$, may be expressed by Eq. (11) for the cationic polymerization of cyclic ethers. Since the changes in basicity and free energy of these ethers can be obtained by Eqs. (2) and (5), Eq. (11) may be rewritten as

$$\log(1/r_n) = \Delta P_{m-n}(\Sigma\sigma^*)_{m\cdot i-n\cdot j} + \alpha\, \Delta(\Delta G)_{(m-n)\cdot 2(\mathrm{CH_3})} + \beta\, \Delta(pK_b)_{(m-n)\cdot 2(\mathrm{CH_3})} + \gamma \qquad (12)$$

where

$$\Delta P_{m-n}(\Sigma\sigma^*)_{m\cdot i-n\cdot j} = (\alpha a_m + \beta b_m) \sum_i \sigma^* - (\alpha a_n + \beta b_n) \sum_j \sigma^* \qquad (13)$$

The comparison between the values of $1/r_1$ (the last two columns in Table 3) calculated by Eq. (12) and observed ones (the 12th column in Table 3) shows good agreement in both values to establish the availability of empirical equation of (11) and (12).

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Zusammenfassung

Die relativen Reaktivitäten von cyklischen Äthern, einschliesslich Epoxiden, Oxetanen, Tetrahydrofuran und Tetrahydropyran, wurden auf Grund ihrer Basizitäten und Freien Energie der Polymerisation abgeleitet. Der Logarithmus der relativen Reaktivität, $1/r_n$, von m-gliedrigen Ringäthern mit i Substituenten und von n-gliedrigen Ringmonomeren mit j Substituenten kann als lineare Kombination der Differenz der Basizitäten $\Delta(pK_b)_{m\cdot i-n\cdot j}$, und der freien Energie, $\Delta(\Delta G)_{m\cdot i-n\cdot j}$, ausgedrückt werden.

$$\log(1/r_n) = \alpha\,\Delta(\Delta G)_{m\cdot i-n\cdot j} + \beta\,\Delta(pK_b)_{m\cdot i-n\cdot j} + \gamma$$

wobei α, β, und γ Konstanten sind. Die Änderungen in der Basizität und der Freien Energie dieser Verbindungen können folgendermassen erhalten werden:

$$\Delta(pK_b)_{m\cdot i-n\cdot j} = b_n \sum_i \sigma^{*} - b_n \sum_j \sigma^{*} + \Delta(pK_b)_{(m-n)\cdot 2(CH_3)}$$

$$\Delta(\Delta G)_{m\cdot i-n\cdot j} = a_m \sum_i \sigma^{*} - a_n \sum_j \sigma^{*} + \Delta(\Delta G)_{(m-n)\cdot 2(CH_3)}$$

hierbei sind a_k und b_k ($k = m, n$) Konstante, σ^* ist die polare Taft'sche Substituentenkonstante und $\Delta(X)_{(m-n)\cdot 2(CH_3)}$ ($X = \Delta G$, pK_b) sind die Differenzen in der Basizität und der Freine Energie zwischen dimethyl-substituierten Verbindungen aus m- und n-gliedrigen Ringen.

Résumé

On a evalué les réactivitiés relatives, les basicités et l'énérgie libre de polymérisation des éthers cycliques, epoxydes compris, de l'oxétane, du tetrahydrofurane, et du tetrahydropyrane. On peut exprimer le logarhitme de la réactivité relative $1/r_n$, des éthers avec m-cycles et des substituants i aux monomères possedants n-cycles et des substituants j, par une combinaison linéaire des différences de basicité $\Delta(pK_b)_{m\cdot i-n\cdot j}$ et d'énérgie libre $\Delta(\Delta G)_{m\cdot i-n\cdot j}$, comme

$$\log(1/r_n) = \alpha\, \Delta(\Delta G)_{m\cdot i-n\cdot j} + \beta\, \Delta(pK_b)_{m\cdot i-n\cdot j} + \gamma$$

ou α, β, et γ sont des constantes. On peut obtenir le changement de basicite et d'énérgie libre de ces composés comme

$$\Delta(pK_b)_{m\cdot i-n\cdot j} = b_m \sum_i \sigma^* - b_n \sum_j \sigma^* + \Delta(pK_b)_{(m-n)\cdot 2(CH_3)}$$

$$\Delta(\Delta G)_{m\cdot i-n\cdot j} = a_m \sum_i \sigma^* - a_n \sum_j \sigma^* + \Delta(\Delta G)_{(m-n)\cdot 2(CH_3)}$$

Ici a_k et b_k ($k = m, n$) sont des constantes, σ^* est le substituant polaire constant de Taft, et $\Delta(X)_{(m-n)\cdot 2(CH_3)}$ ($X = \Delta G$, pK_b) sont des différences de basicité et d'énérgie libre entre les composés dimethyl substitués et des m- et n-cycles, respectivement.

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