

largest K and $|\Delta H|$ with DOMA, indicative that the strongest H bonding occurs in this system, as expected. However, within the haloform series the $|\Delta H|$ values drop but slightly from CHCl_3 through CHBr_3 while the ΔS 's become less negative resulting in an overall increase in K . This could possibly be explained in terms of an increasing amount of "soft" charge-transfer interaction between the N and Br atoms. The charge-transfer interaction will be relatively weaker than the H-bonding interaction and will occur at relatively longer intermolecular separations, thus being less affected by the steric environment of the N atom.

It is worth noting at this point that, while the interpretations of the measured thermodynamic association constants outlined above may be reasonably valid, in fact thermodynamic data *per se* yield no evidence concerning the presence or absence of weak complexes in a system. Evaluation of the extent of complex formation depends on some kind of plausible molecular model. The information obtained (in this case, equilibrium constants) is only as reliable as the model from which it is deduced. In terms of the molecular model invoked here the equilibrium constants obtained from the glc data represent the fractions of molecules which exist as distinct 1:1 "complexes," whether of the H-bonded type, the charge-transfer type, or both. With regard to evidence from other sources as to the existence of these complexes, we have already pointed out¹ that, in addition to the well-documented evidence for C-H

hydrogen bonding to tertiary amines, charge-transfer bands have been observed in solutions containing a tertiary amine together with a variety of halomethanes.² Again, the observation of a charge-transfer band does not in itself prove the existence of 1:1 complexes in solution. However, taken together with the values for the association constants obtained from the glc data, it seems, at least for the amine/halomethane systems (if not for the thioether systems), that complexes other than simple H-bonded ones are found in these solutions and that charge-transfer forces are responsible for at least part of their stabilization.

It would, of course, be of great interest to pursue further studies of these systems (*e.g.*, by spectroscopic techniques) in an effort to resolve the "mixed" association constants into the individual contributions from the different types of complexes. Despite the well-known difficulties involved with the extraction of accurate thermodynamic parameters for weak intermolecular complexes from spectroscopic data, it seems likely that at least the hydrogen-bonding contribution could be evaluated fairly accurately by a careful spectroscopic study. This question will be addressed in more detail in a subsequent publication.⁸

Acknowledgment. This research was supported by a grant from the National Science Foundation.

(8) Paper VI in this series: J. P. Sheridan, D. E. Martire, and S. E. O'Donnell, *J. Amer. Chem. Soc.*, submitted for publication.

Radical Stabilization Energies in Esters. The α -Carbomethoxy Group from Kinetics of the Thermal Isomerization of 1-Chloro-4-carbomethoxybicyclo[2.2.0]hexane in the Liquid Phase

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Abstract: The thermal isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane has been studied in the liquid phase over the temperature range 76–137°. Good first-order kinetics were obtained and the rate constants were well represented by the Arrhenius equations $\log(k_a/\text{sec}^{-1}) = (13.65 \pm 0.07) - (30.16 \pm 0.12)/\theta$, $\log(k_b/\text{sec}^{-1}) = (13.58 \pm 0.12) - (30.00 \pm 0.21)/\theta$, and $\log(k_c/\text{sec}^{-1}) = (13.08 \pm 0.26) - (29.14 \pm 0.45)/\theta$, where $\theta = 2.303RT$ kcal/mol, the error limits are the least-squares deviations, and the subscripts a, b, and c refer respectively to nitrobenzene, diphenyl ether, and tetrachloroethylene as solvent. From these Arrhenius parameters and transition state estimates for a biradical mechanism, the radical stabilization energy of an α -carbomethoxy group is shown to be 4.0 ± 1.7 kcal/mol relative to a hydrogen atom. This is in excellent agreement with a stabilization energy of 4.0 ± 1.9 kcal/mol that we have derived from a single rate of isomerization of 1,4-dicarbomethoxybicyclo[2.2.0]hexane measured independently of this work. The magnitude of this stabilization energy is discussed in terms of polarity effects in radical structures for esters and ketones as strong evidence for a biradical intermediate in the thermal isomerization of bicyclo[2.2.0]hexanes.

An understanding of free-radical chemistry is greatly facilitated by the use of the concept of stabilization (or resonance) energies. By the use of stabilization energies and appropriate standard models, it has

been possible to test the self-consistency of the kinetic parameters for a wide variety of free-radical reactions.²

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(2) (a) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); (b) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS 21, National Standards Reference Data Series, U. S. Dept. of Commerce, Washington, D. C., 1970.

In general, the stabilization energy of a free radical may be defined as the deviation in the ΔH_f° (radical) from that of the standard model. The value of the concept of stabilization energies lies in this definition as a relative quantity and such data are essential in radical chemistry in mechanistic interpretations and synthetic planning. From standard kinetic parameters and stabilization energies, it is possible to calculate experimental activation energies without any knowledge of standard heats of formation for the individual species.

Provided the appropriate standard models are chosen, a theoretical interpretation may be placed on the stabilization energy in terms of electron delocalization and bonding in the radical. The allyl radical is an excellent example and has provided the focus for much theoretical³ and experimental^{2a} study. Although a stabilization energy of 10 ± 1 kcal/mol for the allyl radical has now been obtained from several independent studies,^{2a,4} attempts to fix a stabilization energy for the analogous acetyl and methylacetyl radicals are plagued with gross discrepancies in the experimentally derived values.⁵ There are two explanations for these discrepancies. The first is that the experimental Arrhenius parameters for one or more of the studies are incorrect. The second is that either the standard model or the assumptions in deriving the stabilization energy are not appropriate.

If we consider acetyl resonance in $R\dot{C}HCOOR'$ radicals from carboxylic acids derivatives, the only quantitative estimate of the resonance energy is that derived from the Arrhenius parameters for the thermal decomposition of carbomethoxycyclobutane.⁶ By comparison with the Arrhenius parameters for the ring opening of cyclobutane^{7,8} the carbomethoxy group stabilizes the intermediate 1,4-diradical by 6 kcal/mol at 700°K relative to a hydrogen atom. This may be compared with a stabilization energy of 8.8 kcal/mol (700°K) for the methylacetyl radical obtained from the kinetics of the unimolecular decomposition of ethyl cyclobutyl ketone⁹ or 5.7 kcal/mol (300°K) from the kinetics of iodine atom abstraction from methyl ethyl ketone.⁵

In view of the importance of radical stabilization energies, the bicyclo[2.2.0]hexane system would appear to enable such data to be accurately and readily obtained. In previous papers,¹⁰ we have shown that the thermal isomerization to hexa-1,5-dienes proceeds cleanly at relatively low temperatures with no side reactions. The three mechanisms that may be considered for this isomerization are a two-step biradical mechanism, a symmetry-allowed⁸ concerted $\sigma 2_s + \sigma 2_a$ process, and the symmetry-forbidden ($\sigma 2_s + \sigma 2_s$) concerted mechanism. There is no chemical or theoretical evidence to support the last alternative, and it will not be considered further.

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971).

(5) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(6) M. Zupan and W. D. Walters, *J. Amer. Chem. Soc.*, **86**, 173 (1964).

(7) C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953).

(8) R. W. Carr and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).

(9) B. C. Roquette and W. D. Walters, *ibid.*, **68**, 1606 (1964).

(10) (a) E. N. Cain, *Tetrahedron Lett.*, 1865 (1971); (b) E. N. Cain and R. K. Solly, *J. Amer. Chem. Soc.*, **94**, 3830 (1972); (c) E. N. Cain and R. K. Solly, *Int. J. Chem. Kinet.*, **4**, 159 (1972); (d) E. N. Cain and R. K. Solly, *Aust. J. Chem.*, **25**, 1443 (1972).

We have previously¹⁰ discussed the steric restraints on the ($\sigma 2_s + \sigma 2_a$) process in bicyclo[2.2.0]hexane with respect to the analogous ring-opening reaction of cyclobutane. It was concluded that the biradical mechanism would probably be preferred in the bicyclic system. On this basis, we have previously calculated the stabilization energies of the chloro, bromo, and methoxymethyl substituents. Values obtained for chlorine^{10b} and bromine^{10c} were found to be in good agreement with values obtained from independent studies in completely unrelated systems, while a destabilization by the methoxymethyl group^{10d} showed good analogy with a similar destabilization obtained from the methoxyl C-H bond strength of methyl esters.¹¹ Such self-consistency is in itself good evidence for a biradical mechanism.

In order to further increase the self-consistency of this approach, we here report a detailed kinetic study of the unimolecular decomposition of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane in various solvents. From the assumptions of the biradical mechanism, this will enable us to calculate the stabilization energy of the α -carbomethoxy group. This thermochemical information is important in understanding the decomposition reactions of esters and for considering the theoretical question of resonance in radicals α to π systems containing heteroatoms.

The rate of ring opening of 1,4-dicarbomethoxybicyclo[2.2.0]hexane has been previously reported at a single temperature by Bloomfield.¹² No attempt was made to consider Arrhenius parameters in this work. However, our earlier work¹⁰ on comparison of Arrhenius *A* factors and the variation of rates between the gas phase and various solvents has shown consistent trends. This enables us (*vide infra*) to calculate a value for the $R\dot{C}HCOOCH_3$ radical from this independent work for comparison with our experimental value from the 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane system.

After our original manuscript was submitted, Goldstein and Benzon¹³ reported the thermal inversion of *exo*-2,3,5,6-*d*-bicyclo[2.2.0]hexane. Our interpretation of this interesting work differs from that of the authors in that we are able to show (*vide infra*) that the results can be interpreted as providing strong evidence for a biradical intermediate. In fact, if we rule out "bridge flipping" as postulated by Gassman¹⁴ as a possible inversion mechanism, the inversion may be regarded as conclusive evidence for a biradical mechanism. We are therefore grateful for the opportunity to discuss these results in this revised paper.

Experimental Section

1-Chloro-4-carbomethoxybicyclo[2.2.0]hexane was prepared as previously described by Dauben, Chitwood, and Scherer.¹⁵

Apparatus and Procedure. This was similar to that previously described.^{10b} The rate of isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane was determined in solution (*ca.* 15%) in nitrobenzene-*d*₅, diphenyl ether, and tetrachloroethylene. Sealed nmr tubes were heated by suspending them in refluxing liquid thermostats. The reaction was quenched at measured time intervals

(11) R. K. Solly and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 509 (1971).

(12) D. C. Owsley and J. J. Bloomfield, *J. Org. Chem.*, **36**, 3768 (1971).

(13) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119 (1972).

(14) P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971), ref 26.

(15) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *J. Amer. Chem. Soc.*, **90**, 1014 (1968).

Table I. Rate Constants for the Isomerization of 1-Chloro-4-carbomethoxybicyclo[2.2.0]hexane

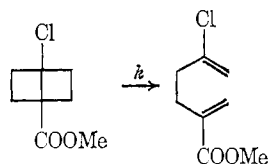
	Temp, °C							
	75.9	82.0	92.6	99.0	108.8	113.8	123.0	137.1
$k \times 10^6 \text{ sec}^{-1}$	0.605 ^a	1.28 ^a	4.16 ^a	8.75 ^a	25.0 ^a	43.2 ^a	104 ^a	394 ^a
$k \times 10^6 \text{ sec}^{-1}$	0.715 ^c	1.32 ^b	4.38 ^c	8.95 ^b	25.6 ^c	43.6 ^b	104 ^c	394 ^b

^a Nitrobenzene-*d*₅ as solvent. ^b Diphenyl ether as solvent. ^c Tetrachloroethylene as solvent.

by immersing the nmr tubes in cold water. All bicyclohexane-diene mixtures were analyzed by integration (mean of three scans) of the ¹H nmr absorptions in the developing olefinic and diminishing aliphatic regions of the spectrum as previously described.^{10b} In addition, integration of both the olefinic signals and the aliphatic signals against the CO₂CH₃ signal(s) as an internal standard provided an independent check on all calculations.

Results

The thermal isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane proceeded cleanly with the formation of only one reaction product. No additional products were apparent in the gas chromatographs of the reaction mixture analyzed on Apiezon-L or SE-30 as the stationary phase. The ¹H nmr of the product isolated by preparative gas chromatography was identical with that previously reported for 2-chloro-5-carbomethoxyhexa-1,5-diene.¹⁶



The rate of decomposition was determined graphically from plots of log (per cent of undecomposed reactant) against time. These plots showed no curvature for at least six different reaction times and to more than 85% isomerization. Rate constants were measured in nitrobenzene-*d*₅, diphenyl ether, and tetrachloroethylene and are shown in Table I.

Rate constants determined in the three solvents were identical at the higher temperatures. However, at the lower temperatures, rates measured in nitrobenzene were slower than those in diphenyl ether, which in turn were slower than the rates in tetrachloroethylene. These differences were much greater than the error limits for the reproducibility of the system but may be inside the systematic error. The variation in rate at the lower temperatures is reflected in the Arrhenius plot for the points shown in Figure 1.

The Arrhenius equations computed by the method of least squares were as follows

$$\log (k_a/\text{sec}^{-1}) = (13.65 \pm 0.07) - (30.16 \pm 0.12)\theta$$

$$\log (k_b/\text{sec}^{-1}) = (13.58 \pm 0.12) - (30.00 \pm 0.21)\theta$$

$$\log (k_c/\text{sec}^{-1}) = (13.08 \pm 0.26) - (29.14 \pm 0.45)\theta$$

where $\theta = 2.303RT$ kcal/mol and the subscripts a, b, and c refer to nitrobenzene, diphenyl ether, and tetrachloroethylene, respectively, as the solvent. The error limits are standard deviations from the least-squares calculations. Their low order of magnitude is a reflection of the reproducibility of the system over the experimental variation of 650-fold in the measured rate constants.

(16) K. V. Scherer, *Tetrahedron Lett.*, 5685 (1966).

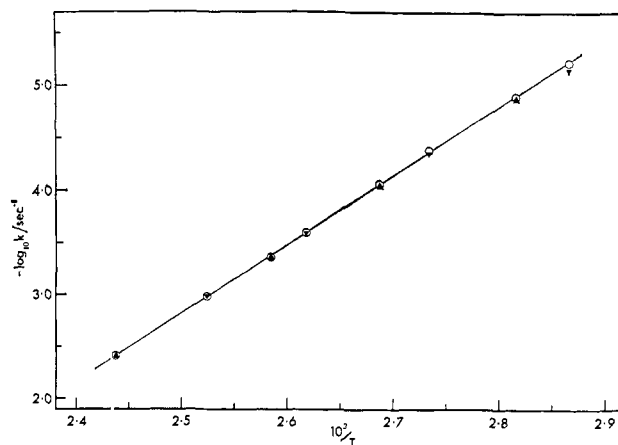
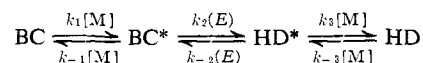


Figure 1. Arrhenius plot for the isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane to 2-chloro-5-carbomethoxyhexa-1,5-diene: (O) in nitrobenzene-*d*₅; (▲) in diphenyl ether; (▼) in tetrachloroethylene.

Discussion

The recent report of ring inversion in the bicyclo[2.2.0]hexane series¹³ sheds new light on the mechanism of the thermal isomerization to hexa-1,5-dienes. Goldstein and Benzon consider that the inversion may occur either *via* a concerted process or through an intermediate biradical. A direct inversion process most likely requires a transition complex in which the bridgehead carbon atoms pass through a planar tetravalent configuration. The energy required for the conversion from tetrahedral to planar tetravalent carbon in methane has been computed to be 127,¹⁷ 187,¹⁷ and 249¹⁸ kcal/mol by Hückel, CNDO, and *ab initio* calculations, respectively. From this analogy, the activation energy for the inversion of the two bridgehead carbon atoms in bicyclo[2.2.0]hexane would be 201, 321, or 445 kcal/mol after subtracting the 53 kcal/mol strain energy present in the ground-state molecule. The discrepancy between the lowest value (from the most simple Hückel calculation) and the experimental activation energy is such that inversion *via* planar bridgehead carbon atoms may be discounted.

Inversion may also be considered to occur *via* a possible transition complex for concerted rearrangement of bicyclo[2.2.0]hexane to hexa-1,5-diene. The complete kinetic scheme for this process is as follows



BC and HD are ground-state bicyclo[2.2.0]hexane and hexa-1,5-diene molecules related by $\Delta H(\text{BC}-\text{HD}) = +10$ kcal/mol.^{2b} BC* and HD* are excited molecules containing energy at least 34 kcal/mol above that of BC;

(17) R. Hoffmann, R. Alder, and C. F. Wilcox, *J. Amer. Chem. Soc.*, 92, 4992 (1970).

(18) H. J. Monckhorst, *Chem. Commun.*, 1111 (1968).

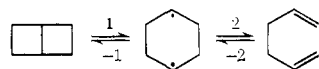
k_1 and k_{-3} are second-order rate constants for the formation of excited molecules, while k_{-1} and k_3 are the corresponding collision rate constants for deactivation back to the ground state; k_2 and k_{-2} are first-order rate constants for the reactions of excited molecules containing energy (E). The general unimolecular rate constant for conversion of BC to HD is given by¹⁹

$$\int_{E_0}^{\infty} \frac{k_1[M]k_2(E)}{k_{-1}[M] + k_2(E)}$$

if $k_{-2}(E)$ is assumed to be zero, and an analogous expression for the conversion of HD to BC. These assumptions are not essential to the calculations but the presentation is greatly complicated if they are not included. Using the standard RRKM formulations,¹⁹ values were computed for all the above rate constants²⁰ by assigning frequencies to BC*, BC* \equiv HD*, and HD* by analogy with published data for cyclobutane, hexane, cyclohexane, butene, and bicyclo[1.1.1]pentane, that for BC and HD not being available.²¹

At 430°K, the overall rate constant for conversion of HD to BC is $5 \times 10^{-17} \text{ sec}^{-1}$ in the pressure-independent region above 10^{-9} Torr. Thus the back reaction of ground-state HD does not offer a plausible route for the inversion of BC. Another possibility is the situation discussed by Lin and Laidler²² in their theoretical treatment of thermal isomerizations. Inversion will occur if the back reaction of excited HD* molecules (formed from BC*) is faster than the rate of collisional deactivation, $k_3[M]$. The above calculations show that at a pressure of 1 Torr, $k_{-2}/k_3[M]$ is 10^{-11} . Inversion by this mechanism is only possible at pressures below 10^{-10} Torr.

These conclusions are as expected from the thermochemistry of the BC-HD system. We have computed the individual rate constants in order to confirm that there are no plausible routes for the inversion of BC by a concerted mechanism. It may be concluded that the thermal inversion of BC occurs *via* a biradical intermediate.



This is the kinetic scheme as used in our previous papers.¹⁰ We have previously assumed $k_{-2} \ll k_{-1} < k_2$, whereas the results of Goldstein and Benzon¹³ indicate $k_{-1} \geq k_2$ and $E_2 \geq E_{-1}$. The observed rate constant is now

$$k_{\text{obsd}} = k_1 k_2 / (k_{-1} + k_2) \quad (1)$$

and the transition complex may be placed between the biradical and HD, rather than between BC and the biradical. However, it should be noted that regardless of the position of the transition complex, it is bound by the constraint that $\Delta S^\ddagger \sim 0 \text{ cal}/(\text{deg mol})$. This would indicate that all the restrictions of the bicyclic structure remain in the transition complex.

The activation parameters calculated for bicyclo[2.2.0]hexane¹³ yield $E_2 - E_{-1} = 1.6 \pm 1.3 \text{ kcal/mol}$ and

(19) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(20) The authors are grateful to Professor B. S. Rabinovitch who originally supplied the subroutines used in these calculations.

(21) Full details of these calculations will be supplied on request.

(22) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 94 (1968).

$k_{-1} = 2k_2$ at 430°K. Substituting $k_2 = mk_{-1}$ in eq 1

$$k_{\text{obsd}} = K_1 k_2 / (1 + m) \quad (2)$$

where K_1 is the equilibrium constant for the biradical and $m = 0.5$ at 430°K. Neglecting the temperature variation in the denominator of eq 2, the experimental activation energy is equal to $\Delta E_1 E_2$, where ΔE_1 refers to the biradical equilibrium, and E_2 is an activation energy. Comparison of ΔE_1 as the substituents on the 1 and 4 positions are varied is a direct measurement of the stabilization energy. In order to obtain this from the experimental activation energy, it is necessary to consider the variation of E_2 with 1,4-substituents. There are no data available for this type of very low-activation energy/highly exothermic reaction. To a first approximation we will consider that E_2 is independent of substituents. Any error in this assumption will be reflected in the value of the stabilization energy derived by this method.

It may be noted that the alternate substitution of $k_{-1} = nk_2$ in eq 1 will yield

$$k_{\text{obsd}} = k_1 / (1 + n) \quad (3)$$

where $n = 2$ at 450°K. While this expression may appear more simple than eq 2, the temperature dependence in the denominator is greater for $E_2 > E_{-1}$. From eq 3, the experimental activation energy may be equated to E_1 . ΔE_1 is obtained by considering the variation in E_{-1} , which for the ring closure of 1,4-biradicals is relatively insensitive to 1,4-substituents and varies only as the number of gauche interactions in forming the 1-4 bond.^{2b}

For $k_{-1} \sim k_2$ and $E_2 \sim E_{-1}$, either of the two forms of eq 1 will yield stabilization energies which agree within $\pm 1 \text{ kcal/mol}$. For example, in our previous paper on the thermal isomerization of 1,4-dichlorobicyclo[2.2.0]hexane,^{10b} the form of eq 3 was used, whereas the latest evidence would suggest that eq 2 will yield smaller errors. The derivation of the stabilization energy from eq 3 incorporates a gauche interaction of 1 kcal/mol in E_{-1} . From eq 2 this will not influence ΔE_1 and consequently the experimental activation energy (the effect will be to decrease $E_2 - E_{-1}$). The stabilization energy from the two chlorine atoms will be reduced from 3.1 to 2.1 kcal/mol and the stabilization energy per chlorine atom to $1.05 \pm 1.0 \text{ kcal/mol}$.

As discussed in the previous section, the experimental activation energy measured in this work may be equated to $\Delta E_1 E_2$. For comparison with the parent hydrocarbon, it is necessary to standardize this to the gas phase at 298°K. We have previously shown that in the liquid phase there is an increase in the rate of bicyclo[2.2.0]hexane isomerizations (maximum of 100%) with respect to the gas phase.¹⁰ Most of this difference is found in the activation energy, it being reduced by $1 \pm 1 \text{ kcal/mol}$ below that measured in the gas phase. From the experimental activation energy in nitrobenzene, E_a (gas phase, 380°K) for the 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane system is $31 \pm 1 \text{ kcal/mol}$.

In order to consider the stabilization energy at 298°K, the temperature variation of E_a is required. This is most readily obtained by considering the Arrhenius pre-exponential factor, since both C_p° and S° have a func-

tional dependence on the same molecular parameters. From eq 1

$$\log A = \log (ekT/h) + (\Delta S_1 + \Delta S_2^\ddagger)/2.303R - \log (1 + k_2/k_{-2}) \quad (4)$$

at 400°K, $\log (ekT/h)$ is 13.35, so that the experimental $\log A$ of 13.65 in nitrobenzene would indicate that $\Delta S_1 + \Delta S_2^\ddagger$ is ~ 0 cal/(deg mol). The structure of the transition complex must be similar to that of the reactant molecule and the temperature variation of E_a will be insignificant. The experimental activation energy with respect to gas phase at 298°K is 31 ± 1 kcal/mol.

By a similar argument, the activation energy for the parent hydrocarbon is also temperature independent. The activation energy for the isomerization to hexa-1,5-diene has been reported to be 36.0,²³ 36.2,²⁴ and 36.8¹³ kcal/mol. If we compare the mean value of 36.3 ± 0.5 kcal/mol with that derived in this work, the difference of 5.2 ± 1.1 kcal/mol may be ascribed to the decrease in ΔE_1 . The variation in ΔE_1 is dependent upon the relative stability of both the reactants and the biradicals. The major factor affecting the relative stability of the bicyclo[2.2.0]hexane molecule is the additional 1,4-chlorine-carbomethoxy cis interaction. Analogous substituents in the cis and trans alkene series²⁵ suggest this is likely to be 0 kcal/mol.

All of the reduction in ΔE_1 may be considered as the stabilization energy of 1-chloro-4-carbomethoxy substituents on the cyclohexane 1,4-biradical.

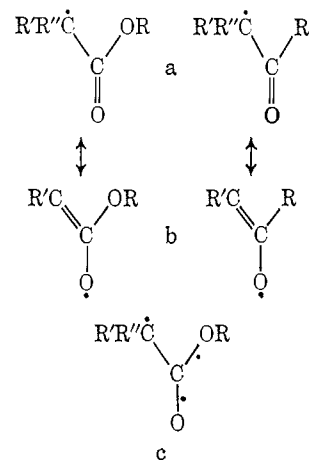
As calculated (*vide supra*), the stabilization energy per chlorine atom derived from the kinetics of the isomerization of 1,4-dichlorobicyclo[2.2.0]hexane and eq 2 is 1.05 ± 1.0 kcal/mol. This is based on an activation energy of 36.0 kcal/mol for the parent hydrocarbon²³ as obtained in the original measurement of this system. Taking into account the two subsequent measurements increases the mean activation energy to 36.3 kcal/mol and consequently the stabilization energy per chlorine atom to 1.2 ± 1.0 kcal/mol. Subtracting this stabilization energy from the total stabilization energy of the 1-chloro-4-carbomethoxycyclohexane 1,4-biradical, the stabilization energy of the carbomethoxy group is 4.0 ± 1.5 kcal/mol with respect to the gas phase at 298°K.

We may also calculate a stabilization energy from the single rate of isomerization of 1,4-dicarbomethoxybicyclo[2.2.0]hexane reported by Bloomfield.¹² The Arrhenius A factor is again likely to be within the range $10^{13.5 \pm 0.5} \text{ sec}^{-1}$. Combined with the experimental rate constant at 348°K, this yields an activation energy of 27.3 ± 0.8 kcal/mol. Since Bloomfield and Owsley's rate was measured in chloroform, the addition of 1 ± 1 kcal/mol will yield the activation energy with reference to the gas phase. Compared to bicyclo[2.2.0]hexane, the effect of the 1,4-carbomethoxy groups is to decrease the activation energy by 9.0 ± 1.6 kcal/mol. To obtain the stabilization energy in the biradical this activation energy decrease must be corrected for the instability introduced into the reactant molecule by the *cis*-1,4-

carbomethoxy interaction. This is 1 ± 1 kcal/mol with reference to *cis*-1,2-dimethylcyclobutane.²⁶ Thus the radical stabilization energy per carbomethoxy group is found to be 4.0 ± 1.9 kcal/mol with respect to a hydrogen atom. This is in excellent agreement with the value obtained in this present work from 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane, although it may be noted that there is a difference of $10^{2.6} \text{ sec}^{-1}$ in the rate of decomposition at 348°K.

This stabilization energy may be compared with the analogous stabilization energy in the methylacetyl radical of 5.7 ± 1.7 kcal/mol.⁵ Although the difference of 2.2 kcal/mol could be accommodated within the error limits of both measurements, it is in good agreement with expected polarity effects^{10d} introduced by the differences in electron distribution between ketones and esters. Electron diffraction²⁷ and microwave²⁸ measurements show the alkoxy C–O bond of esters to have 20% double bond character in terms of bond length, although there is no reduction in the double bond character of the carbonyl bond. The effect of this electron concentration in the alkoxy C–O bond is to polarize the electron distribution around the carbonyl carbon. Thus the alkyl substituent on this carbon is adjacent to a more positive and hence less screened nucleus compared to the analogous ketones. This effect is most pronounced on the α bond strength, where the C–H bond strength is increased from 87 kcal/mol in ketones to 93 kcal/mol in formates.²⁹ The effect is attenuated in the inductive transfer of the positive character to the β carbon atom, where the C–H bond strength in esters is 1.7 kcal/mol greater than in ketones.

An alternate description of the stabilization energy is obtained by considering electron delocalization in the



R = alkyl; R', R'' = H or alkyl

radicals a–c. Structures a and b have been considered for the methylacetyl radical,⁵ where it was shown that b was 20 kcal/mol less stable than a. However, the resonance structure, formed by mixing the wave functions of a and b was stabilized by 2.5 kcal/mol with respect to the nonresonance structure. As discussed earlier, there is a significant contribution from valence bond structure c to the structure of ester molecules.

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This implies there is a mixing of the wave functions from structures a and c in the ester radical, in preference to structures a and b, which leaves the relative stability of the radical unchanged.

Previous discussion has been confined to discussion of the stabilization energy with respect to a hydrogen atom. For consideration of resonance energies arising from electron delocalization, it is more appropriate to compare the rate with respect to the corresponding alkyl substituent. In alkanes, C-H bond strengths show a uniform decrease of 98, 95, and 92 kcal/mol for the formation of primary, secondary, and tertiary radicals.^{2b} Similarly, C-C bond strengths in ethane, propane, and butane (2-3 bond) show the same uniform decrease of 88, 85, and 82 kcal/mol, respectively.^{2b} Alkyl substitution in the position β to the breaking bond does not affect the bond strength, the 1-2 bond strength of butane being 85 kcal/mol. To a good approximation, substitution of a hydrogen atom by a carbon atom decreases the α -bond strength by 3 kcal/mol.

On this basis, the radical resonance energy of the α -carbomethoxy group is only 1.0 kcal/mol. This is not unreasonable compared with a similarly defined resonance energy of 2.7 kcal/mol in the methylacetyl radical.⁵ The difference is due to the effect of structure c in reducing the additional electron delocalization.

Conclusion

The radical stabilization energy of an α -carbomethoxy group has been shown to be 4.0 ± 1.7 kcal/mol as derived from the solution kinetics for the isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane with respect to a hydrogen atom; a calculation based upon the reported isomerization of 1,4-dicarbomethoxybicyclo[2.2.0]hexane yields an identical value of 4.0 ± 1.9 kcal/mol. The excellent agreement between these values is strong support for the accuracy of the reported rates of isomerization of bicyclo[2.2.0]hexane, 1,4-dichlorobicyclo[2.2.0]hexane, 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane, and 1,4-dicarbomethoxybicyclo[2.2.0]hexane, which were measured in five independent laboratories, and the assumptions of the biradical mechanism used in the derivation of the stabilization energies. Furthermore, the relative magnitude of the stabilization energy compared with 5.7 ± 1.7 kcal/mol in the methylacetyl radical⁵ is in good agreement with known differences in the bonding of esters and ketones. It should be noted that this stabilization energy in the methylacetyl radical was derived from the rate of reaction between iodine and methyl ethyl ketone and incorporates none of the assumptions of the biradical mechanism.

Conformational Analysis. II. The Molecular Structure, Composition, and Trans-Gauche Energy and Entropy Differences and Potential Hindering Internal Rotation of Gaseous Oxalyl Bromide as Determined by Electron Diffraction¹

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Abstract: Gaseous oxalyl bromide has been studied by electron diffraction at nozzle temperatures of 6, 80, and 211°. As in the case of oxalyl chloride, reported earlier, the molecules exist as a mixture of trans and gauche conformers instead of trans and cis as had been previously supposed. The "bent" single bond pair concept of the double bond accounts nicely for the instability of the cis form relative to the gauche. Assuming that the conformers differ only in their torsion-angle values, the values of some of the more important parameters at 6° with estimated errors of 2σ are $r_{C=O} = 1.177$ (0.003) Å, $r_{C-C} = 1.546$ (0.008) Å, $r_{C-Br} = 1.925$ (0.004) Å, $\angle CCO = 124.6$ (0.5)°, $\angle CCB r = 111.6$ (0.5)°, ϕ (the gauche torsion angle relative to 0° for the trans form) = 114.1 (19.9)°, $l_{C=O} = 0.0337$ (0.0053) Å, $l_{C-C} = 0.0450$ Å (assumed), $l_{C-Br} = 0.0480$ (0.0069) Å, and δ (the rms torsion amplitude for the trans conformer) = 30.7 (7.6)°. The mole fractions of the trans conformer at 6, 80, and 211° are 0.480 (0.095), 0.423 (0.099), and 0.359 (0.124), respectively, from which the energy difference ($\Delta E^\circ = E_g^\circ - E_t^\circ$) and the entropy difference ($\Delta S^\circ = S_g^\circ - S_t^\circ$) are calculated to be 0.63 kcal/mol ($\sigma = 0.32$) and 1.1 cal deg⁻¹ mol⁻¹ (0.9). The experimental results allow the determination of the rotational potential function assumed to be of the form $2V = V_1(1 - \cos \phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi)$; the values of the coefficients are $V_1 = 0.62 \pm 0.27$, $V_2 = 0.20 \pm 0.19$, and $V_3 = 0.43 \pm 0.21$, all in kcal/mol. The heights of the barriers separating the trans from the gauche and the gauche from the gauche forms are 0.78 ± 0.43 and 0.48 ± 0.31 kcal/mol, respectively. The predicted value for the torsional frequency of the trans form is 35 cm⁻¹, which is in good agreement with the observed 40 cm⁻¹.

In a recent article¹ we reported the results of an electron-diffraction investigation of oxalyl chloride vapor. Among these results was the mildly surprising

(1) For paper I of this series see K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 1003 (1973).

discovery that the vapor consists of substantial amounts of a gauche ($\phi \approx 125^\circ$) conformer instead of the s-cis ($\phi = 180^\circ$) in equilibrium with the s-trans ($\phi = 0^\circ$) form; interpretations of spectroscopic data,² which on

(2) See ref 1 for a summary.