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The kinetics and mechanism of the reaction between carbon dioxide and a series of amines Observation and interpretation of an isokinetic effect

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Abstract

Kinetics investigations have been made on the reaction of some organic amines with dimethylcarbonate (DMC) in the presence of carbon dioxide. *N*-alkyl-carbamates were formed and measurements were made for a series of substituents in the amine. Second-order kinetics was used in the analysis.

The rate constants have been analyzed and the resulting Arrhenius parameters indicate an isokinetic effect. The stepwise increase of the activation energies and the value of the isokinetic temperature are such that the selective energy transfer (SET) model suggests a δ(COC) vibration mode of the dimethylcarbonate to be activated in the rate determining reaction step. The DMC molecule is hydrogen bonded to the quartenary ammonium cation. The energy source is suggested to be a closely related vibration mode of the dimethylcarbonate serving as solvent.

Keywords: Selective energy transfer (SET) model; Carbon dioxide; Carbamates; Dimethylcarbonate; Catalysis

1. Introduction

The reaction between primary amines and dialkylcarbonates has been studied for the development of new synthetic ways to organic carbamates [1–4]. The process is of industrial interest.

The reaction between primary or secondary amines and dialkylcarbonates has previously been described [5] as requiring a suitable catalyst (Lewis acids, Rh or Ru metal complexes) for observing satisfactory conversion rates and high selectivities to carbamates. According to our findings [6,7], carbon dioxide a cheap, abundant and non-toxic species which does not present regeneration and recycling problems, plays an effective catalytic role in this reaction:

$$RNH_2 + OC(OMe)_2 \xrightarrow{CO_2(cat.)} RNHC(O)OMe + MeOH \quad (1)$$

Reaction (1) can be understood so that [RNH_3]-[O_2CNHR], prepared in situ from aliphatic primary amines and carbon dioxide, reacts with dimethyl carbonate (DMC) to give *N*-alkyl-methylcarbamates.

$$2\,RNH_2 + CO_2 = RNH_3{}^+\,{}^-O_2CNHR \quad (2a)$$

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$$RNH_3{}^+{}^-O_2CNHR + DMC \rightarrow RNHC(O)OMe + CO_2 + RNH_2 + MeOH \quad (2b)$$

In this reaction, CO_2 is produced again, and thus, a catalytic circle is established. Reaction (1) can be carried out in common organic solvents, but more easily, the organic carbonate, in this case DMC, may be employed as the reaction medium. Satisfactory reaction rates and good selectivities can be attained by heating the reaction mixture at temperatures between 323 and 363 K, under CO_2 pressure (pCO_2 = 0.1–0.2 MPa). Under controlled conditions, ureas, *N*,*N*-substituted carbamates, secondary and tertiary amines are formed in very low amounts, if any [6,7].

Using $^{13}CO_2$ we have shown [7] that the reaction involves two steps. *O*-carbomethoxylation of the carbamate anion is the first step to give a mixed carbamic–carbonic anhydride, RNHC(O)OC(O)OMe. The decarboxylation of RNH*C(O)OC(O)OMe through the expulsion of the carbamic CO_2 molecule is very selective and leads to the formation of RNHC(O)OMe. This suggested mechanism rationalizes the lack of incorporation of $^{13}CO_2$ in the organic carbamate using $RNH_3{}^+{}^-O_2$ $^{13}CNHR$ or $^{13}CO_2$ and amine.

Kinetics investigations have now been made for a series of substituents in the amine. The aim of the investigation was to test if the SET model [8] could predict the mechanism of the process. The reaction has been measured in excess of dimethylcarbonate and at constant pressure of CO_2, as will be described below. The following substituents R were selected: C_6H_5–CH_2–, *cyclo*-C_6H_{11}–, *n*-C_3H_7–, *iso*-C_4H_9–, *sec*-C_4H_9–, *n*-C_4H_9–, and CH_2=CH–CH_2–.

2. Experimental part

2.1. General methods

All reactions and manipulations were carried out under dinitrogen or carbon dioxide atmosphere by using vacuum line techniques. DMC (from Fluka) was dried over activated molecular sieves 4A (24 h), filtered and, then, distilled under dinitrogen. Diethylether was distilled from Na/$Ph_2C(O)$. All the used amines were from Fluka (puriss., >99.5%). DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and methylchloroformate were Janssen and Aldrich products, respectively. CO_2 (99.995%) was from Air Liquide.

GC analyses in kinetic experiments were carried out with a HP 5890 Series II gas chromatograph equipped with a RSL-150 capillary column (30 m × 0.25 mm Bonded FSOT). GC–MS analyses were performed with an HP 5890 gas-chromatograph (capillary column: SE-30; 30 m × 0.25 mm) connected with a HP 5970 selective mass detector. IR spectra were obtained with a Perkin-Elmer 883 spectrophotometer. ^1H NMR spectra were recorded with a Bruker AM 300 or 500 spectrometer and calibrated (in ppm versus TMS) with respect to the solvent peak.

2.2. Synthesis and characterization of carbamates

Carbamates RNHC(O)OMe (*R* = C_6H_5–CH_2–; *cyclo*-C_6H_{11}–; *n*-C_3H_7–; *iso*-C_4H_9–; *sec*-C_4H_9–; *n*-C_4H_9–; CH_2=CH–CH_2–), used as standards in kinetics experiments, were prepared according to the procedure described in [7] (*R* = C_6H_5–CH_2–; *cyclo*-C_6H_{11}–; CH_2=CH–CH_2–) or by reaction of the corresponding amine RNH_2 (1 mol) (*R* = *n*-C_3H_7–; *iso*-C_4H_9–; *sec*-C_4H_9–; *n*-C_4H_9–) with methylchloroformate (1 mol) in the presence of DBU (1 mol) as a base, in diethylether as solvent, at 273 K (reaction time: 3 h). According to the latter procedure, the (DBUH)Cl salt precipitated was separated by filtration and eliminated and the mother solution evaporated in vacuo. The carbamate RNHC(O)OMe (*R* = *n*-C_3H_7–; *iso*-C_4H_9–; *sec*-C_4H_9–; *n*-C_4H_9–) was isolated as liquid pure by distillation of the residue.

The full characterization of *N*-benzyl-, *N*-allyl- and *N*-cyclohexyl-methylcarbamate has been reported elsewhere [7]. Below, we report the spectroscopic characterization of the other carbamates RNHC(O)OMe (*R* = *n*-C_3H_7–; *iso*-C_4H_9–; *sec*-C_4H_9–; *n*-C_4H_9–) here investigated.

2.2.1. Characterization of n-C_4H_9NHC(O)OMe

IR (neat, KBr disks): 3341 (s, broad), 1708 (vs), 1534 (vs), 1254 (vs), 1193 (m-s), 1143 (s), 1112 (m-s), 1056 (m-s), 1023 cm^{-1} (s). ^1H NMR ($CDCl_3$, 300 MHz, 293 K): δ 0.75 (3H, t, $^3J_{HH}$ = 7.25 Hz, CH_3), 1.19 (2H, m, CH_2), 1.32 (2H, m, CH_2), 3.00 (2H, slightly broad quartet, $^3J_{HCCH}$ = $^3J_{HCNH}$ = 6.5 Hz, NCH_2), 3.48 (3H, s, OCH_3), 5.14 (1H,

broad, N*H*). MS (*m*/*z*): 131 ($M^{+\bullet}$), 116, 102, 88, 76, 59, 44.

2.2.2. Characterization of iso-C_4H_9NHC(O)OMe

IR (neat, KBr disks): 3337 (m-s, broad), 1702 (vs), 1534 (vs), 1252 (vs), 1145 (s), 1018 cm^{-1} (s). ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 0.82 (6H, d, $^3J_{HH}$ = 6.66 Hz, (CH_3)$_2$C–), 1.67 (1H, m, C*H*), 2.90 (2H, d, $^3J_{HH}$ = 6.88 Hz, NCH_2), 3.58 (3H, s, OCH_3), 4.87 (1H, broad, N*H*). MS (*m*/*z*): 131 ($M^{+\bullet}$), 116, 100, 88, 74, 59, 44.

2.2.3. Characterization of sec-C_4H_9NHC(O)OMe

IR (neat, KBr disks): 3329 (s, broad), 1703 (vs), 1533 (vs), 1276 (s), 1242 (vs), 1193 (m-s), 1165 (m-s), 1096 (s), 1027 (m-s), 1000 cm^{-1} (s). ^{1}H NMR ($CDCl_3$, 500 MHz, 293 K): δ 0.83 (3H, t, $^3J_{HH}$ = 7.46 Hz, CH_2CH_3), 1.05 (3H, d, $^3J_{HH}$ = 6.60 Hz, $CHCH_3$), 1.38 (2H, m, CH_2), 3.54 (1H, broad unresolved multiplet, NC*H*), 3.58 (3H, s, OCH_3), 4.6 (1H, broad, N*H*). MS (*m*/*z*): 131 ($M^{+\bullet}$), 116, 102, 84, 70, 58, 41.

2.2.4. Characterization of n-C_3H_7NHC(O)OMe

IR (neat, KBr disks): 3338 (m-s, broad), 1711 (vs), 1529 (vs), 1267 (vs), 1193 (s), 1141 (s), 1049 cm^{-1} (s). ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K): δ 0.83 (2H, t, $^3J_{HH}$ = 7.42 Hz, CH_3), 1.43 (2H, m, CH_2), 3.05 (2H, t, slightly broad, $^3J_{HH}$ = 7.08 Hz, NCH_2), 3.58 (3H, s, OCH_3), 4.87 (1H, broad, N*H*). MS (*m*/*z*): 117 ($M^{+\bullet}$), 102, 88, 76, 70, 59, 44.

2.3. Kinetics experiments: experimental procedure

A 0.8 ml of anhydrous DMC (stored under dinitrogen), the amine (*V* ml) and undecane (as internal standard; 0.006 ml, 0.0284 mmol) were introduced into a 6 ml vial under a carbon dioxide stream. The following volumes *V*(ml) were used for the amines, respectively:

n-butylNH$_2$	0.072 ml (0.7265 mmol);
iso-butylNH$_2$	0.074 ml (0.7376 mmol);
sec-butylNH$_2$	0.074 ml (0.7305 mmol);
allylNH$_2$	0.054 ml (0.7216 mmol);
n-propylNH$_2$	0.060 ml (0.7268 mmol);
cyclo-hexylNH$_2$	0.062 ml (0.7218 mmol);
benzylNH$_2$	0.078 ml (0.7148 mmol).

After saturating the system with CO_2 (0.1 MPa, r.t. (288 K)), the vial was closed with a screwcap equipped with a silicone septum through which the reaction mixture could be sampled using a GC syringe.

It is worth noting that, except for the case of *sec*-butylamine, a white precipitate, (RNH$_3$)O$_2$CNHR, was formed upon saturation with CO_2. This precipitate however, dissolved in the reaction solvent (DMC) at the temperature used during the kinetic run.

In order to take into account the fact that minor amounts of carbamate RNHC(O)OMe can form directly in the GC-injection chamber (473 K) and to correct for this effect, a micro-volume of the reaction mixture, before heating to the reaction temperature, was injected in the GC. The amount of carbamate formed directly in the GC-injector was so evaluated.

The reaction system was then heated to the appropriate temperature. After a given time, the reaction mixture was rapidly cooled to room temperature and a micro-volume of solution withdrawn with a syringe and analyzed by GC. The vial was then heated again to the working temperature. The analysis was repeated at suitable intervals of time.

Data were corrected for the reaction in the GC injection chamber and the corrected values used for a second-order kinetic analysis (Fig. 1). Results are

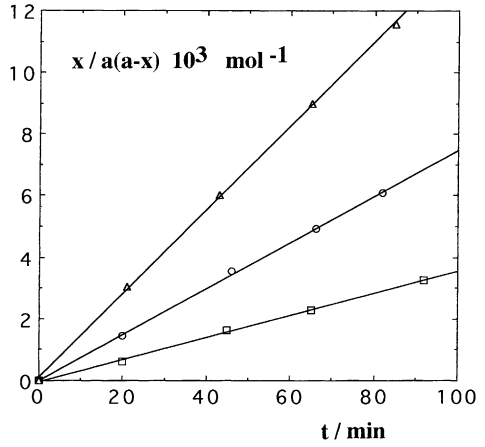

Fig. 1. Example of the kinetic analysis. The system is *sec*-butylamine. The quantity $x/a(a-x)$ is plotted against time and the slope of the lines are transformed to rate constants with the dimension $M^{-1}\,h^{-1}$; a is the number of mmol amine at the start and x is the number of mmol of carbamate formed. The temperatures in the example are 334.16, 343.16 and 353.16 K, respectively.

reported in Table 1. For most of the amines, the readings at 363 K were discarded as they gave a less good value of r^2 (r = correlation coefficient of the linear relation in the kinetics equation).

3. Results

The rate constants reported in Table 1 were plotted against $1/T$ in an Arrhenius diagram and the activation energies could be calculated from the slopes of the Arrhenius lines. The resulting values are given in Table 2.

One notes from Table 2 that the activation energies for *iso*-butylamine and *n*-propylamine are almost the same. In order to avoid confusion when demonstrating the Arrhenius lines (Fig. 2), we have used the six points from the two systems to define one common line (this is denoted $k2 + k5$).

Table 1
The second-order rate constants, k, and their temperature dependence

Amine	Temperature T (K)	$k \times 10^2$ ($M^{-1} h^{-1}$)
n-Butylamine	334.2	2.00
	344.2	4.70
	354.2	12.4
	364.2	21.4
iso-Butylamine	333.2	1.12
	344.2	3.75
	352.2	8.1
sec-Butylamine	334.2	0.187
	343.2	0.391
	353.2	0.71
Allylamine	324.2	0.80
	334.2	1.68
	345.2	2.75
	353.2	3.82
n-Propylamine	333.2	1.10
	344.2	4.03
	354.2	11.1
cyclo-Hexylamine	354.2	0.72
	360.2	0.77
	366.2	0.85
Benzylamine	344.2	4.06
	356.2	5.3
	361.2	5.8

One of the aims of the present investigation is to apply the model of selective energy transfer, SET [8], to the kinetic data of the amine DMC reaction. As the analysis of isokinetic effects is a major field of the application of the SET model [8], it is of interest to assess if the Arrhenius lines define an isokinetic point or not. From Fig. 2 one can identify three groups of lines, the first one containing $k1$ and $k2 + k5$; the second one is made up by $k3$ and $k6$, and the last one is made up by $k4$ and $k7$. As pointed out by Linert [9] the method of analyzing the Arrhenius lines is superior to the commonly used procedure of plotting the logarithm of the preexponential factor against E_a.

Realizing, also, that there sometimes appears a difference in the ordinate of what should, per definition of the isokinetic effect, be a common point of intersection [10], we can try to analyze the three groups as if they would have one and the same abscissa value of their respective points of intersection. By taking the mean of the abscissa values for the intersections of ($k1$ and $k2 + k5$), ($k3$ and $k6$) and ($k4$ and $k7$), respectively, we end up with a probable value of an isokinetic temperature, $1/T_{iso} = (2.81 \pm 0.03)\ 10^{-3}\ K^{-1}$ or $T_{iso} = 356 \pm 4$ K. It should be noted that if one instead of $k1$ and $k2+k5$ uses the mean of intersections of $k1$ with the lines describing $k2$ and $k5$ separately one will achieve the same result, $1/T_{iso} = (2.81 \pm 0.03)\ 10^{-3}\ K^{-1}$.

4. Discussion

4.1. SET formalism

The important figure that comes out from the analysis above is $T_{iso} = 356 \pm 4$ K. Can we apply the SET model to describe the magnitude of T_{iso}?

As described previously [8], the SET model treats the resonance transfer of energy from vibrations of the catalyst system ($\omega\ cm^{-1}$) to one vibration mode of the reactant molecule ($\nu\ cm^{-1}$).

For a perfect resonance ($\omega = \nu$) it has been derived that the isokinetic temperature can be expressed as

$$T_{iso} = \frac{Nhc\nu}{2R} = 0.719\nu \quad (4)$$

where N, c, h, R are constants of nature and ν is expressed in cm^{-1}. In the absence of full resonance, the

Table 2
Activation energies and the treatment to indicate the stepwise change[a]

Amine	E_a (kcal mol^{-1})	r^{2b}	$E_a - RT$ (kcal mol^{-1})	Δ' (kcal mol^{-1})[c]	n'[d]	n[e]
n-Butylamine	19.6	0.9921	18.9	14.4	10	13
iso-Butylamine	24.3	0.9996	23.6	4.7	3	16
sec-Butylamine	16.5	0.9946	15.8	7.8	5	11
Allylamine	12.1	0.9855	11.4	4.4	3	8
n-Propylamine	25.8	0.9993	25.1	13.7	9	17
cyclo-Hexylamine	3.7	0.9944	3.0	22.1	15	2
Benzylamine	5.2	0.9966	4.5	1.5	1	3
Total				68.6	46	

[a] Tentative value of the increment:

$$\Omega' = \frac{\sum \Delta'}{\sum n'} = \frac{68.6}{46} = 1.49 \pm 0.04\,\text{kcal mol}^{-1} = 521 \pm 14\,\text{cm}^{-1}.$$

[b] r^2 is the correlation coefficient of the Arrhenius graphs (e.g. Fig. 1). The effective temperature has been set to 340 K, and consequently, the term $RT = 0.7\,\text{kcal mol}^{-1}$ has been used throughout the calculations.

[c] Δ' means the absolute values of the consecutive difference between the $E_a - RT$ data (1 kcal = 4.184 kJ).

[d] n' is a subjective estimate of the number that the smallest of the Δ values (1.5) is contained in the Δ' concerned.

[e] n indicates the number of vibration levels contained in $E_a - RT$.

following relation between ν and ω has been deduced [8]:

$$T_{iso} = NhcR^{-1}(\nu^2 - \omega^2)\omega^{-1} \times \left\{ \frac{\pm\pi}{2} - \text{arctg}(0.5\nu\,\omega(\nu^2 - \omega^2)^{-1} \right\}^{-1} \quad (5)$$

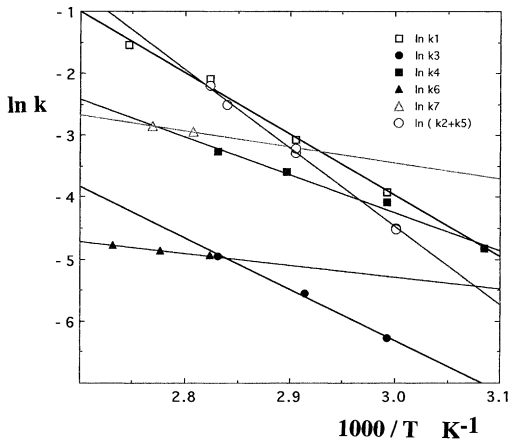

Fig. 2. The Arrhenius graphs for the investigated systems as reported in Table 1. The numbers refer to the substituents as follows: 1 = *n*-butyl; 2 = *iso*-butyl; 3 = *sec*-butyl; 4 = allyl; 5 = *n*-propyl; 6 = *cyclo*-hexyl; 7 = benzyl ($k2 + k5$ means a line correlating all six points from systems 2 and 5. The third point of system 2 is hidden by an adjacent point of system 5).

If we apply this formalism to the experimental finding of $T_{iso} = 356 \pm 4$ K, we obtain from the simple formula (4) $n = 495 \pm 6\,\text{cm}^{-1}$. This value — if full resonance is operating — should correspond to one of the vibration modes that is present in the mixture of quaternary ammonium carbamate and dimethyl carbonate, i.e. the reactants of relation (2b). One might note that the C–O–C bending mode of DMC, 518 cm^{-1} [11], is very close to this first guess.

4.2. Activation energies

In order to get an independent idea about the magnitude of ν, one can analyze the values of activation energies (Table 2). After correction by the term RT these values seem to form a series of data changing stepwise with a constant increment (that we call Ω [12] here) or with a multiple of this increment.

This is in accordance with the SET treatment [12] and the appropriate relation is

$$E_a - RT = n\nu + \nu x n^2 \quad (6)$$

or

$$\frac{(E_a - RT)}{n} = \nu + \nu x n \quad (7)$$

where ν has the same meaning as above, x is the anharmonicity parameter and n is the vibrational quantum number.

The accuracy of the data and the number of measurements are not that high that we can apply the approach SETOS developed by Jamroz and coworkers [12], but we have to rely on a less refined method developed in [13].

This means that the difference between consecutive $E_a - RT$ are formed and the most reasonable estimate for a natural number in the ratio of $\Delta(E_a - RT)$/(the smallest of these data) is introduced in column 6 of the Table 2 as n'. In the present case, $\Delta(E_a - RT)_{\text{smallest}} = 1.5\,\text{kcal mol}^{-1}$.

Then the sum of the absolute values of $\Delta(E_a - RT)$ is divided by the sum of the thus estimated n'. This gives us a tentative value of the increment Ω' between successive activation energies. In the last column of Table 2 we give the number (n) that the increment Ω' is contained in the respective $E_a - RT$ values. This is presented only to exemplify the concept of vibrational excitation. The limited accuracy of the measurements makes it not possible to use the full treatment of Eq. (7).

Hence, we chose to neglect the second term of Eq. (7) representing the anharmonicity of the vibration mode in question and put $\nu = \Omega' = 1.49\,\text{kcal mol}^{-1} = 521\,\text{cm}^{-1}$. This value should be compared to the data from infrared spectroscopy. The C–O–C bending mode is assigned by Collingwood and Wilmhurst [11] to $518\,\text{cm}^{-1}$. This is indeed very close to the value found above and consequently we might infer that the C–O–C bending mode of DMC is the critical mode for the rate determining step.

4.3. Isokinetic temperature

We noted above that the isokinetic analysis in the case of full resonance should result in a critical vibration mode corresponding to $495 \pm 6\,\text{cm}^{-1}$. As this is very close to the value we found from the above analysis of the activation energies ($521 \pm 14\,\text{cm}^{-1}$), one can conclude that full resonance is almost at hand. The small differences can be accounted for by the spread of experimental errors and — above all— by the non-identity of the three sets of lines of Fig. 2.

One might suggest that the energy donor (ω in our notation, cf. Eq. (5)) is the C–O–C bending mode of the free solvent DMC molecules, whereas the critical ν of the reacting DMC molecule has a slightly different value as it is closely bonded to the ion pair of the quaternary ammonium carbamate. The geometry of such an interaction is depicted in Fig. 3. The arrow indicates the probable direction of attack of an oxygen atom of the carbamate anion on the central, positive carbon atom of DMC. As the ion pair is approaching, when the C–O–C angle is increasing and the hindering CH_3 group is moving away, a hydrogen bond between the quaternary cation and the nearest oxygen of the DMC is formed. This H-bond opens up a reactive pathway for the splitting off of a molecule of methanol

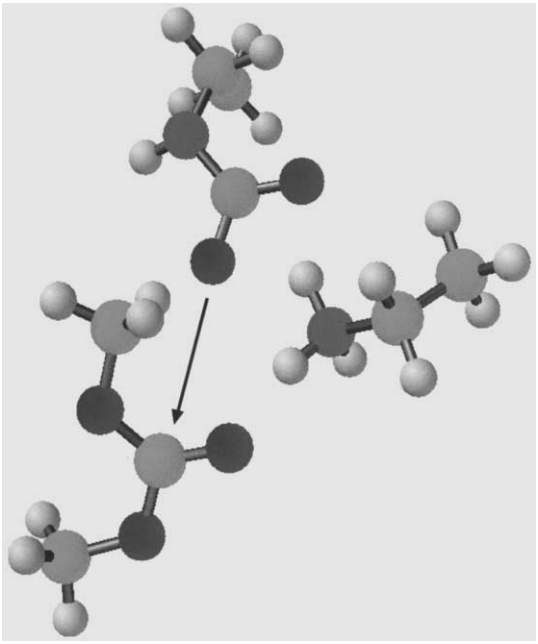

Fig. 3. The interaction between the carbamate ion pair and a molecule of DMC. The substituents R are indicated by an ethyl group, R = C_2H_5. The repulsive interaction between the amine substituents positions these groups at the far end of the reaction scene. The reaction probably implies an attack by the nearest carbamate oxygen on the central carbon of the DMC molecule (indicated by an arrow). One can see that the upper CH_3 group is a hindrance for the approach of the carbamate ion to the DMC central carbon atom. The optimization of the structure was performed using the PM3 method [14], within the NDDO approximation. The following hydrogen bonds were found: between NH_3^+ and CO_2–, the H···O distances are 1.754 and 1.811 Å (one H-atom interacts with both O-atoms) and between the NH_3^+ group and the carbonate C=O group the H···O distance is 1.795 Å.

as indicated in reaction formula (2b). Simultaneously, a molecule of the amine is released. Later the carbamate CO_2 (i.e. the catalyst) is split off [7].

The strong variation of activation energies with the size and form of the substituent R might be related to the repulsive/attractive interactions between this group, in the cation and anion, and the methyl group(s) of the DMC molecule defining the structure of the ion pair-solvent cage system. The easier it is for the two molecules to approach each other, the smaller should be the need for adjusting the position of the methyl groups and thus the smaller will be the activation energy. The more one has to push away the methyl group(s) by activating the δ(COC) mode, the higher the activation energy will be.

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References

[1] M. Aresta, E. Quaranta, Chem. Tech. 27 (3) (1997) 32, and references therein.
[2] M. Aresta, A. Dibenedetto, E. Quaranta, Tetrahedron 54 (1998) 14145.
[3] M. Aresta, A. Dibenedetto, E. Quaranta, Green Chem. 1 (1999) 237.
[4] M. Aresta, A. Dibenedetto, E. Quaranta, B. Marciniec, Appl. Organomet. Chem.14 (2000) 1.
[5] F. Porta, S. Cenini, M. Pizzotti, C. Crotti, Gazz. Chim. Ital. 115 (1985) 275.
[6] M. Aresta, E. Quaranta, Ital. Patent 1,237,207 (1993).
[7] M. Aresta, E. Quaranta, Tetrahedron 47 (1991) 9489.
[8] R. Larsson, J. Mol. Catal. 55 (1989) 70.
[9] W. Linert, Chem. Phys. 129 (1989) 381.
[10] G.C. Bond, Z. Phys. Chem. NF 144 (1985) 21.
[11] H.L. Collingwood, J.K. Wilmhurst, Aust. J. Chem. 19 (1966) 1637.
[12] R. Larsson, M.H. Jamroz, M.A. Borowiak, J. Mol. Catal. A: Chem. 129 (1988) 41.
[13] R. Larsson, Catal. Today 4 (1989) 235.
[14] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.