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Thermolysis kinetics of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates

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An experimental approach was developed to determine the intrinsic thermolysis rate constants of the central carbon–carbon bond during the *dl*/*meso* isomerization of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates (G=H, Me, OMe, Cl, and NO_2) at temperatures ranging from 80 to 120 °C. The obtained rate constants are significantly affected by the polarity of the *para* substituents, in sharp contrast to their negligible effects on the *dl*/*meso* isomerization equilibrium constants. Moreover, the substituent effects on the activation enthalpies can be linearly correlated with the Hammett substituent resonance constants and the homolytic dissociation enthalpies (bond dissociation energies) of the benzylic C–H bonds of ethyl 2-cyano-2-(*p*-substituted phenyl)acetates. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this paper.

Keywords: activation enthalpy and entropy; *dl*/*meso* thermal isomerization; hexasubstituted ethane; thermolysis kinetics, polymerization initiators

INTRODUCTION

The central carbon–carbon (C–C) bond strength (reactivity) of hexasubstituted ethane is significantly influenced by the size and electronic structures of the substituents. For example, the C–C bond dissociation enthalpy (BDE) of ethane is well established to be 377.4 ± 0.8 kJ/mol,[1,2] while the central C–C BDE of the hypothetical hexaphenylethane is estimated only in the range of 50–70 kJ/mol.[3,4] The difference of ~310 kJ/mol in bond strength corresponds to a reactivity difference of 10^{54} times at 25 °C. The tremendous difference explains why hexaphenylethane is thermodynamically unstable even at room temperature, while the decomposition of ethane into methyl radicals with $t_{1/2} = 1.0$ h occurs only at a temperature of around 690 °C,[3–5] although the true structure of the hypothetical hexaphenylethane is 3-triphenylmethyl-6-diphenylmethylidene-1, 4-cyclohexadiene, which could be further isomerized into 1-diphenylmethyl-4- triphenylmethylbenzene.[5]

The reactivities (stabilities) of hexasubstituted ethanes can be tuned by a variation of the substituents.[3,4,6] Aiming at the synthesis of polymerization initiators, we have synthesized a series of hexasubstituted ethanes from the copper-mediated oxidative coupling of ethyl 2-cyano-2-(*p*-substituted phenyl) acetates as shown in Scheme 1. The *dl* and *meso* diastereomeric mixtures of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl) succinates (**1**) were separated and then characterized by nuclear magnetic resonance (NMR), infrared, ultraviolet and mass spectrometry analyses,[7,8] and their stereochemical structures were confirmed by X-ray crystal structure analysis.[9] Although the central C–C bond lengths are longer (~1.60 Å) than the standard (1.54 Å),[9] the *dl* and *meso* diastereomers are both stable, indicating that the corresponding homolysis into diradicals is negligible at room temperature. However, these *dl* and *meso* diastereomers have been demonstrated as excellent polymerization initiators at ~100 °C for various alkene monomers such as styrene, acrylonitrile, methyl mathacrylate, etc.[8–10]

The thermolysis rate constants of the central C–C bond homolysis are important for the applications of hexasubstituted ethanes as polymerization initiators. Ruchardt and Beckhaus[3,4] have developed a series of methods to determine the thermolysis rate constants of the central C–C bond homolysis for hexasubstituted ethanes and some of their *meso* and *dl* diastereomers. Bennett *et al.*[11] have employed a similar approach to determine the thermolysis rate constants for the *meso* and *dl* diastereomers resulting from the photoreduction of 5,6-dihydro-3,5,5-trimethyl-1,4-oxazin-2-one. However, these thermolysis rate constants were exclusively obtained by the addition of radical scavengers, followed by the quantification of the hydrogen abstract products as shown in Scheme 2. Weiner[12] has demonstrated that the addition of radical scavengers could significantly affect the thermolysis rate constants and the differences could be over 30 times. Moreover, small or even negative activation entropies were generally observed from the central C–C bond homolysis studies,[3,4,11,12] suggesting that the added radical scavenger may involve the C–C bond thermolysis because a unimolecular reaction should have a substantial positive activation entropy because of the much looser transition state.[13] This is not unexpected because the radical scavengers can only trap the escaped radical intermediates rather than the radical intermediates in the solvent cages. In the present paper, we present a unique experimental approach to determine the intrinsic thermolysis rate constants without the need for any radical scavengers for the central C–C bond

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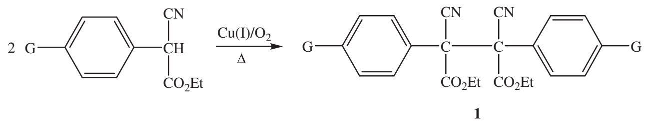

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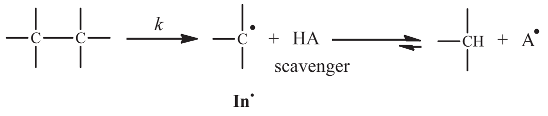
G = *p*-H; *p*-Me; *p*-OCH$_3$; ***p*-Cl and *p*-NO$_2$**

Scheme 1. Synthesis of diethyl 2,3-dicyano-2,3-di(p-substituted phenyl) succinates



Scheme 2. Kinetics of the carbon-carbon bond homolysis

homolysis of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl) succinates (G=H, Me, OMe, Cl and NO$_2$) at various reaction temperatures.

RESULTS AND DISCUSSION

The *dl*/*meso* isomerization of diethyl 2,3-dicyano-2,3-diphenylsuccinate (G=H, Scheme 1) was examined using a simple reversible reaction model (Eqn (1)) by quantification of the *dl* and *meso* diastereomeric concentrations because the *dl* and *meso* diastereomers have differently well-resolved high-performance liquid chromatography (HPLC) peak retention times, which are summarized together with the retention times of other substituted substrates in Table S1.[8,14] However, the obtained activation entropies from the apparent rate constants were found to be different from negative to positive (−46 to + 30 J/mol·K) in different solvents,[8,14] suggesting that the over-simplified kinetic approach (Eqn (1)) may not be suitable to model the *dl*/*meso* isomerization of diethyl 2,3-dicyano-2,3-diphenylsuccinate.

$$1_{meso} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 1_{dl} \tag{1}$$

Dl/*meso* isomerization

Homolytic cleavage of the central C–C bond is the major and usually the sole pathway for the thermolysis of hexasubstituted ethanes.[3,4,15] The *dl*/*meso* isomerization of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates has been proposed to proceed via the central C–C bond homolysis to yield two radical intermediates (In·) followed by their recombination as shown in Scheme 3.[8,9] Ethyl 2-cyano-2-(*p*-substituted phenyl)acetates were found as the only observed products from the thermolysis of either *meso* or *dl* diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates in the presence of a radical scavenger such as thiophenol.[8,9] The radical intermediates derived from the central C–C bond homolysis were confirmed by the well-resolved electron spin resonance spectrum.[8] The formation of radical intermediates is further supported by the fact that diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates can all be used as radical initiators for various alkene polymerizations.[10]

Kinetic method for *dl*/*meso* isomerization

The *dl*/*meso* isomerization of Scheme 3 can be simply expressed as Eqn (2)

$$1_{meso} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,\mathrm{In}^{\bullet} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 1_{\mathrm{dl}} \tag{2}$$

where k_1, k_2, k_3 and k_4 are the rate constants for the designated elementary step reactions.

The analytic solutions for the reversible first-order consecutive reaction ($A \rightleftharpoons B \rightleftharpoons C$) are known, but they are clearly too complex to process any experimental data without approximation.[16] To the best of our knowledge, no analytic solutions for the reversible bimolecular consecutive reaction (Eqn (2)) have ever been reported in the literature. Nevertheless, we expect that such analytic solutions will be more complex even if the related differential equations could be solved. Thus, it is necessary to develop an approximate approach to process the experimental results.

The rate differential equations for the reactant 1_{meso} and intermediate In$^{\bullet}$ of Eqn (2) are given

$$\frac{\mathrm{d}[1_{meso}]}{\mathrm{d}t} = -k1[1_{meso}] + k2[\mathrm{In}^{\bullet}]^2 \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{In}^{\bullet}]}{\mathrm{d}t} = k1[1_{meso}] + k4[1_{dl}] - k2[\mathrm{In}^{\bullet}]^2 - k3[\mathrm{In}^{\bullet}]^2 \tag{4}$$

where $[1_{meso}]$, $[\mathrm{In}^{\bullet}]$ and $[1_{dl}]$ are the concentrations of 1_{meso}, In$^{\bullet}$ and 1_{dl} at time *t*, respectively.

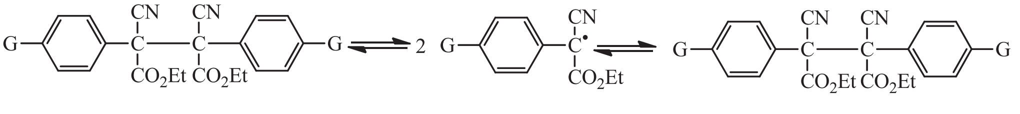
Electron spin resonance studies showed that the concentrations of the radical intermediates were found to be less than 10^{-5} M at temperatures below 120 °C, indicating that the radical concentrations are negligible relative to the *meso* and *dl* diastereomeric concentrations (0.2 ~ 0.3 M) (also refer to the Experimental Section). Thus, the derivative of the radical intermediate concentration (Eqn (4)) should also be negligible. After applying the steady-state approximation to the radical intermediate In$^{\bullet}$, that is, $\mathrm{d}[\mathrm{In}^{\bullet}]/\mathrm{d}t = 0$, rearrange Eqn (4) to yield

$$[\mathrm{In}^{\bullet}]^2 = \frac{k1[1_{meso}] + k4[1_{dl}]}{k2 + k3} \tag{5}$$

Substitution of Eqn (5) into Eqn (3) gives

$$\frac{\mathrm{d}[1_{meso}]}{\mathrm{d}t} = \frac{k2k4[1_{dl}] - k1k3[1_{meso}]}{k2 + k3} \tag{6}$$

Because the radical intermediate concentrations are negligible,



$\mathbf{1_{meso}}$ **In•** $\mathbf{1_{dl}}$

G=*p*-H; *p*-Me; *p*-OMe; *p*-Cl; and *p*-NO2

Scheme 3. DL/MESO Isomerization

the concentration of the product *dl* diastereomer ($[1_{dl}]$) can be obtained from Eqn (7).

$$[1_{dl}] \approx [1_{meso}]_o - [1_{meso}] \tag{7}$$

where $[1_{meso}]_o$ and $[1_{meso}]$ are the *meso* diastereomeric concentrations at times 0 and *t*.

Substitution of Eqn (7) into Eqn (6) yields

$$\frac{\mathrm{d}[1_{meso}]}{\mathrm{d}t} = \frac{k2k4[1_{meso}]_o}{k2+k3} - \frac{(k1k3+k2k4)[1_{meso}]}{k2+k3} \tag{8}$$

Integration of Eqn (8) gives[1b]

$$\ln\{k1k3[1_{meso}] - k2k4([1_{meso}]_o - [1_{meso}])\} = \frac{k1k3+k2k4}{k2+k3}t \tag{9}$$

The *dl/meso* isomerization equilibrium constant (K_{eq}) can be obtained either by forward/backward rate constants or by equilibrated concentrations as shown in Eqn (10).

$$K_{\mathrm{eq}} = \frac{k1k3}{k2k4} = \frac{[1_{dl}]^{\mathrm{eq}}}{[1_{meso}]^{\mathrm{eq}}} \tag{10}$$

where $[1_{dl}]^{\mathrm{eq}}$ and $[1_{meso}]^{\mathrm{eq}}$ are the equilibrated concentrations of 1_{dl} and 1_{meso}, respectively.

Because $[1_{meso}]_o \approx [1_{meso}]^{\mathrm{eq}} + [1_{dl}]^{\mathrm{eq}}$, Eqn (9) can be rewritten as

$$\ln\{[1_{dl}]^{\mathrm{eq}} - [1_{dl}]\} = \frac{k1k3+k2k4}{k2+k3}t = k_{\mathrm{obs}}t \tag{11}$$

where

$$k_{\mathrm{obs}} = \frac{k1k3+k2k4}{k2+k3} \tag{12}$$

Interestingly, Bennett *et al.*[11] derived similar kinetic equations and used them to validate their thermolysis rate constants as determined by the addition of the radical scavenger for the *meso* and *dl* diastereomers.

Thermolysis rate constants for the central C–C bond homolysis

For a complex chemical reaction, it is usually difficult to determine the rate-determining step, resulting in the difficulty to correlate the apparent rate constant with any given elementary step reaction.[17]

The *dl* diastereomers are 11.5 ± 1.3 times more stable than the corresponding *meso* counterparts for diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates regardless of the substituent polarity,[7–9] suggesting that the forward rate constants k_1 and k_3 should be larger than the backward k_2 and k_4 in a similar magnitude. Thus, the apparent rate constant (k_{obs}) should be approximately equal to the thermolysis rate constant k_1 for the central C–C bond homolysis.

$$k_{\mathrm{obs}} = \frac{k1k3+k2k4}{k2+k3} \approx k_1 \tag{13}$$

The experimental error introduced by this approximation can be estimated by Eqn (14) to be less than about 8% because *K* is 11.5 ± 1.3.[8]

$$\Delta k = \frac{k_{\mathrm{obs}} - k_1}{k_{\mathrm{obs}}} = \frac{1-(k_1/k_4)}{1+K} < \frac{1}{1+K} \tag{14}$$

Because the *dl* diastereomers are predominant at equilibrium, the *meso* diastereomers were used for all of the kinetic studies. Figure 1 shows the *dl* and *meso* concentration time courses for the *dl*/*meso* isomerization of diethyl 2,3-dicyano-2,3-di(*p*-methylphenyl)succinate at temperatures of 80, 90, 100, 110, and 120 °C. The *dl* and *meso* concentration time courses for the rest of the diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl) succinates are summarized in the supplementary material. These concentration time courses show that the product *dl*'s concentrations increase as the reactant *meso*'s concentrations decrease and each substrate has its own characteristic isoconcentration at different temperatures. Nice linear correlations were obtained after these concentration time courses were processed according to Eqn (11). The representative linear correlations are summarized in Fig. 2 for diethyl 2,3-dicyano-2,3-di

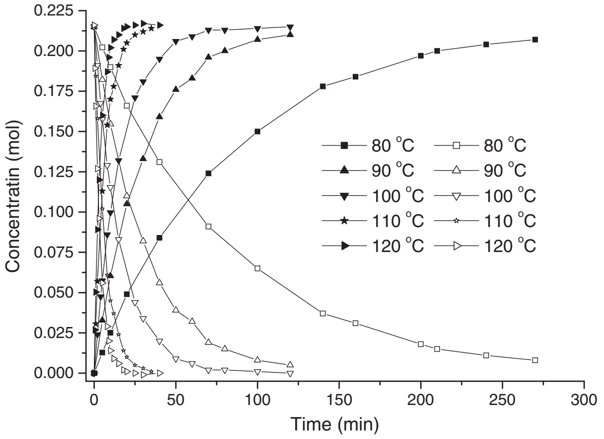


Figure 1. Concentration time courses for diethyl 2,3-dicyano-2,3-di(*p*-methylphenyl)succinate at different reaction temperatures. The lines with unfilled labels are for the *meso* diastereomer and the lines with filled labels are for the *dl* diastereomer

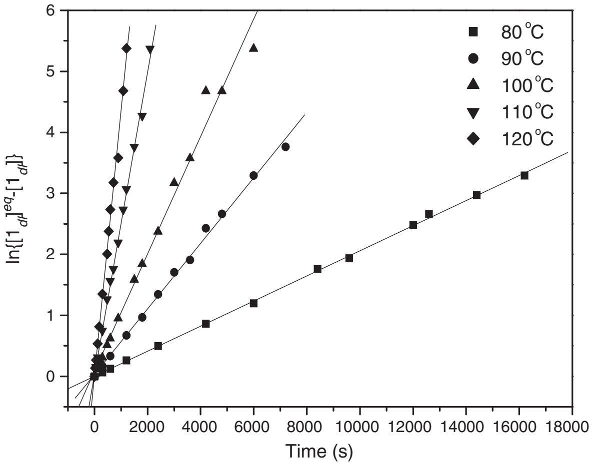


Figure 2. Linear plots of $\mathrm{Ln}\{[1_{dl}]^{\mathrm{eq}} - [1_{dl}]\}$ versus reaction time for diethyl 2,3-dicyano-2,3-di(*p*-methylphenyl)succinate at different reaction temperatures

(*p*-methylphenyl)succinates, and the rest of the linear correlations are summarized in the supplementary material. The resultant thermolysis rate constants (k_1) from the linear correlations are summarized in Table 1 for all diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates at temperatures of 80, 90, 100, 110 and 120 °C.

An examination of Table 1 shows that the introduction of *p*-Me, *p*-MeO, and *p*-Cl groups increase the rate constants by 3–10 times, whereas the introduction of *p*-NO_2 group decreases the rate constants by about two times. At the same reaction temperature, the relative thermolysis rate constants for the five substrates are best correlated with the Hammett resonance constants of the *para*-substituents. Most interestingly, the thermolysis rate constants increase with the reaction temperature by 20–80 times. These results are in sharp contrast to the negligible effects of reaction temperature and *p*-substituents on the *dl*/*meso* isomerization equilibrium constants.[8,9] It is worth noting that the thermolysis rate constants (Table 1) are all much larger than the rate (10^{-4} min^{-1}) of radical formation required for efficient polymerization initiators,[19] suggesting that these hexasubstituted ethanes can be used as polymerization initiators.[10]

Activation parameters for the central C–C bond homolysis

The activation enthalpies and entropies for the central C–C bond homolysis of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl) succinates were obtained from the temperature-dependent rate constants (Table 1) according to the Eyring equation (Eqn (15)),[18] and the related results are summarized in Table 2.

$$\ln(k_1/T) = \ln(k_B/h) + \Delta S^{\neq}/R - \Delta H^{\neq}RT \qquad (15)$$

Table 1. Thermolysis rate constants (k_1) for the central C–C bond of diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates at various reaction temperatures[a]

Temperature	80 °C	90 °C	100 °C	110 °C	120 °C
p-H	0.163	0.615	2.07	6.66	13.3
p-CH_3	1.99	4.48	9.24	24. 7	43.4
p-OCH_3	2.06	5.37	9.63	24.9	43.3
p-Cl	0.723	1.98	5.50	12.7	33.6
p-NO_2	0.0839	0.300	0.877	3.42	7.23

[a] First-order rate constants in min^{-1}. The *dl*/*meso* isomerization reactions were performed in 1,1,2,2-tetrachloroethane solution.

Table 2. Activation enthalpies and entropies for the central C–C bond homolysis for diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates[a]

Substrate	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/mol·K)	Correlation coefficient (r^2)
p-H	126	59.2	0.994
p-CH_3	87.9	48.4	0.996
p-OCH_3	85.0	47.6	0.994
p-Cl	107	54.0	0.999
p-NO_2	128	59.0	0.996

[a] Activation enthalpies and entropies obtained from the thermolysis rate constants according to Eqn (15).

An examination of Table 2 shows that the activation entropies are all similarly positive (53.4 ± 5.8 J/mol·K), which are in good agreement with the unimolecular reaction mechanism for the thermal *dl*/*meso* isomerization (Scheme 3 and Eqn (2)) because a loose transition state is usually characterized by a substantial positive activation entropy.[13] Most intriguingly, the *para*-substituents exert noticeable effects on the activation enthalpies in contrast to their negligible effects on the *dl*/*meso* isomerization equilibrium constants. For example, the introduction of the *p*-NO_2 group increases the activation enthalpy by ~2 kJ/mol, whereas the introduction of the *p*-CH_3, *p*-CH_3O, and *p*-Cl groups decreases the activation enthalpy by 38.5, 41.4 and 19.4 kJ/mol, respectively. The *para*-substituents should have similar steric and inductive effects for the central C–C bond homolysis because they are far away from the reaction centers. Thus, the activation enthalpy differences must be primarily associated with the electronic (resonance) effects of the *para*-substituents through the aromatic ring, which are similar to the substituent effects on the thermolysis rate constants. Indeed, the resultant activation enthalpies are best linearly correlated with the corresponding substituent resonance constants (σ_R), as shown in Fig. 3.

Homolytic bond dissociation enthalpies of the benzylic C–H bonds

The activation enthalpy reflects the stability of the transition state[13] and BDE has long been considered as the best quantitative measure of the radical thermodynamic stability.[21] The linear Hammett correlation of the kinetic results (Fig. 3) prompted us to examine whether the activation enthalpies can be correlated with the thermodynamic stabilities of the radical intermediates. Theoretical calculations have been widely used to obtain BDEs of various chemical bonds.[22] The GAUSSIAN (Pittsburgh PA USA) package with the density function theory was used in this study to calculate the benzylic C–H BDEs (Scheme 4) and the related results are summarized in Table 3.

Table 3 shows that the benzylic C–H BDE of ethyl 2-cyano-2-phenylacetate is 332.5 kJ/mol, which is in excellent agreement with the experimental result (334.5 kJ/mol) that was determined from the equilibrium acidity and oxidation

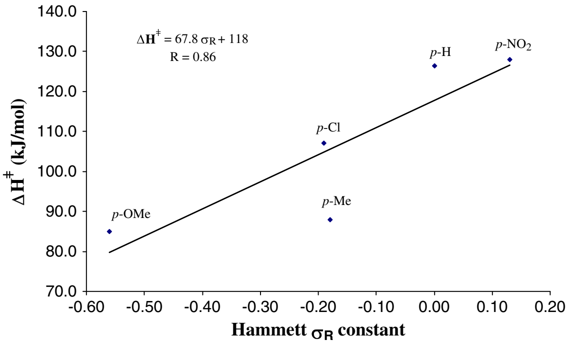
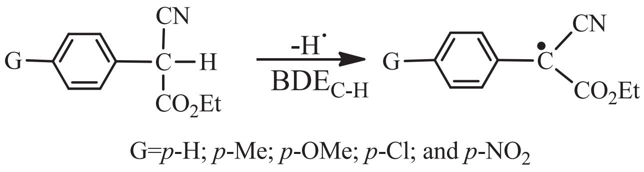


Figure 3. Correlation of the activation enthalpies with the substituent resonance constants (σ_R)[20]



Scheme 4. Benzylic C-H bond dissociation enthalpies

Table 3. Homolytic bond dissociation enthalpies of benzylic C–H bonds of ethyl 2-cyano-2-(*p*-substituted phenyl) acetates[a]

Substrates	$BDE_{C–H}$ (kJ/mol)
p-H	332.5
p-OCH_3	318.3
p-CH_3	325.9
p-Cl	329.1
p-NO_2	335.1

[a]Obtained from the theoretical calculations at the Becke, three-parameter, Lee–Yang–Parr/6-31G* level.

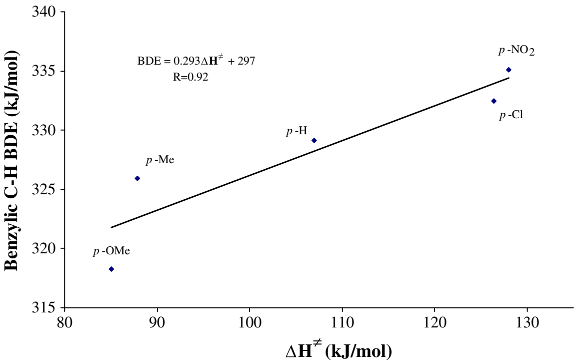


Figure 4. Correlation of the benzylic C–H BDEs with the activation enthalpies

potential measurements.[23] The introduction of the *p*-NO_2 group increases the benzylic C–H BDE, whereas introduction of the *p*-CH_3, *p*-CH_3O, and *p*-Cl groups decreases the benzylic C–H BDEs. These effects are similar to the substituent effects on the activation enthalpies. We have shown that the BDEs of the benzylic C–H, phenolic O–H, and thiophenolic S–H bonds can be linearly correlated with Hammett constants of the substituent on the aromatic ring.[24] Nevertheless, the thermodynamic benzylic C–H BDEs can also be linearly correlated with the kinetic activation enthalpies derived from the central C–C bond homolysis as shown in Fig. 4. These linear correlations confirm that the measured rate constants are the thermolysis rate constants for the central C–C bond homolysis.

CONCLUSIONS

In summary, we have determined the thermolysis rate constants for diethyl 2,3-dicyano-2,3-di(*p*-substituted phenyl)succinates (G = H, Me, OMe, Cl, and NO_2) without the need for any radical scavengers. The activation enthalpies of the central C–C bond homolysis can be linearly correlated with the Hammett substituent resonance constants and the homolytic dissociation enthalpies of the benzylic C–H bonds of ethyl 2-cyano-2-(*p*-substituted phenyl)acetates, which provide the additional evidences to support the reliability of the novel kinetic approach reported in this paper.

EXPERIMENTAL SECTION

Chemicals and instruments

All solvents were of analytical grade, or the highest grade commercially available. 1,1,2,2-Tetrachloroethane (Aldrich, Milwaukee, WI, USA) was soaked in anhydrous $MgSO_4$ overnight and then distilled under a reduced pressure. NMR spectra were recorded on a Bruker AM (Madison, WI, USA) 400 MHz instrument. HPLC analysis was carried out on a Hitachi model (Tokyo, Japan) liquid chromatograph. The quantitative HPLC analysis was employed by the internal standard technique with a calibration against authentic reference compounds.

General synthesis procedure

Diethyl 2,3-dicyano-2,3-diphenylsuccinate, diethyl 2,3-dicyano-2,3-di(*p*-methylphenyl)succinate, diethyl 2,3-dicyano-2,3-di(*p*-chlorophenyl)-succinate and diethyl 2,3-dicyano-2,3-di(*p*-methoxyphenyl)succinate were synthesized using a protocol adapted from the literature procedure, that is, from the reactions of the corresponding *para*-substituted benzylcyanide carbanions with diethyl carbonate, followed by the copper-mediated oxidative coupling reactions.[7,25] Diethyl 2,3-dicyano-2,3-di(*p*-nitrophenyl)-succinate was synthesized from the nucleophilic substitution of *p*-nitrochlorobenzene with ethyl cyanoacetate carbanion, followed by the copper-mediated oxidative coupling reaction.[7,26] The *meso* and *dl* diastereomers were separated by fractional crystallization using a mixed solvent of carbon tetrachloride and ethyl acetate and they were characterized by NMR, mass spectrometry, and HPLC analyses.[7,8]

Kinetic measurements for *dl*/*meso* isomerization

Flasks containing 0.2–0.30 M of the *meso* diastereomers in a 1,1,2,2-tetrachloroethane solution were purged with nitrogen for about 10 min before heating in a pre-equilibrated thermostat (80, 90, 100, 110, or 120 °C). Aliquots were taken and were immediately quenched in a dry ice–acetone bath at different time intervals then subjected to the HPLC analysis.

THEORETICAL CALCULATIONS

Density function theory calculations were performed using the GAUSSIAN-03 program at the Becke, three-parameter, Lee–Yang–Parr/6-31G* level.[27,28]

SUPPORTING INFORMATION

Kinetic concentration time courses and linear correlations for the dl/meso isomerization and Cartesian coordinates and absolute energies for the calculated structures.

Acknowledgements

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REFERENCES

[1] W. M. Haynes, Ed. *CRC Handbook of Chemistry and Physics*, 91st edn, **2010–2011**. (a) 9–73; (b) A-21.

[2] T. Vreven, K. Morokuma, *J. Phys. Chem. A* **2002**, *106*, 6167.

[3] C. Ruchardt, H.-D. Beckhaus, *Angew. Chem. Int. Ed Engl.* **1980**, *19*, 429.

[4] C. Ruchardt, H.-D. Beckhaus, *Top. Curr. Chem.*, **1986**, *130*, S. 1.

[5] J. M. McBride, *Tetrahedron*, **1974**, *30*, 2009.

[6] K. Kornblum, *Angew. Chem. Int. Ed Engl.* **1976**, *14*, 734.

[7] Y.-C. Liu, D.-L. Yang, H.-L. Lu, *Chem. J. Chin. Univ.* **1984**, *5*, 410.

[8] D.-L. Yang, C. Qi, J. Jin, Y.-L. Li, Y.-C. Liu, *Sci. China Ser. B* **1993**, *23*, 1144.

[9] Y.-C. Liu, D.-L. Yang, Q.-C. Yang, Y.-Z. Han, Y.-Q. Tang, *Sci. China Ser. B* **1986**, *4*, 337.

[10] C. Qi, Y. Hu, G. Ji, W. Liu, F. Yan, X. Zheng, *J. Appl. Polym. Sci.* **2001**, *81*, 2964.

[11] R. W. Bennett, D. L. Wharry, T. H. Koch, *J. Am. Chem. Soc.* **1980**, *102*, 2345.

[12] S. A. Weiner, *J. Am. Chem. Soc.* **1971**, *93*, 6978.

[13] C. Lifshitz, *Chem. Soc. Rev.* **2001**, *30*, 186.

[14] S. Gao, X. Zhou, X. Wang, *J. Liq. Chrom. Relat. Tech.* **1998**, *21*, 567.

[15] H. A. P. de Jongh, C. R. H. I. de Jonge, H. J. M. Sinnige, W. J. de Klein, W. G. B. Huysmans, W. J. Mijs, W. J. van den Hoek, J. Smidt, *J. Org. Chem.* **1972**, *37*, 1960.

[16] N. M. Rodiguin, E. N. Rodiguina, *Consecutive Chemical Reactions*, translated by R. F. Schneider, D. Van Nostrand Company, Inc., Princeton, NJ, **1964**, Ch 4.

[17] T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd edn, Harper and Row, New York, **1987**, pp. 190–202.

[18] T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd edn, Harper and Row, New York, **1987**, pp. 208–209.

[19] G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization*, 2nd edn, Elsevier, Oxford, **2006**, p. 64.

[20] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.

[21] F. G. Bordwell, X.-M. Zhang, *Acc. Chem. Res.* **1993**, *26*, 510.

[22] X.-M. Zhang, *J. Org. Chem.* **1998**, *63*, 3590.

[23] X.-M. Zhang, F. G. Bordwell, *J. Phys. Org. Chem.* **1994**, *7*, 751.

[24] F. G. Bordwell, X.-M. Zhang, A. V. Satish, J.-P. Cheng, *J. Am. Chem. Soc.* **1994**, *116*, 6605.

[25] H. A. P. de Jongh, C. R. H. I. de Jonge, W. J. Mijs, *J. Org. Chem.* **1971**, *36*, 3160.

[26] X.-M. Zhang, D.-L. Yang, Y.-C. Liu, *J. Org. Chem.* **1993**, *58*, 224.

[27] M. J. Frisch, G. W. Trucks, H. B. Schelegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. J. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomas, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, M. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. N. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision C. 02, Gaussian, Inc., Pittsburgh PA, USA, **2003**.

[28] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford, New York, **1989**.