

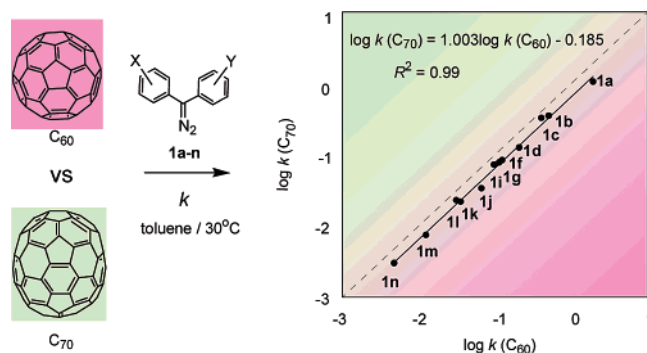
Kinetic Substituent and Solvent Effects in 1,3-Dipolar Cycloaddition of Diphenyldiazomethanes with Fullerenes C₆₀ and C₇₀: A Comparison with the Addition to TCNE, DDQ, and Chloranil

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Kinetics of 1,3-dipolar cycloaddition of a series of meta- and para-substituted diphenyldiazomethanes (DDMs) with fullerenes C₆₀ and C₇₀ as dipolarophiles have been investigated in toluene at 30 °C. Fullerene C₆₀ was ca. 1.5 times more reactive than C₇₀. The rate constants (*k*) for the primary [3 + 2] additions increased with the increase of the electron-releasing ability of the meta and para substituent. The log *k*/*k*₀ values were well correlated by the Yukawa–Tsuno (Y–T) equations with the smaller negative ρ values (–1.6 and –1.7 for C₆₀ and C₇₀) and the reduced resonance reaction constants *r* (0.22 and 0.17) compared to similar reactions of common acceptors, TCNE, DDQ, and chloranil (CA). The plots of log *k* (acceptor) versus log *k* (C₆₀) as reference gave good regression equations and the slopes became larger in the order of TCNE > DDQ > CA > C₇₀ ≥ C₆₀. The rates were also found to decrease with the increase of solvent polarity due to the ground-state solvation of fullerenes. However, the relative reactivity of these acceptors toward the unsubstituted DDM increased in the order of DDQ > C₆₀ ≥ C₇₀ > TCNE > CA. The unexpected higher reactivity of fullerenes was interpreted in terms of the inherent steric strain by the pyramidalization of the sp² C-atoms as well as the shorter [6,6] bonds with larger π -electron densities.

Introduction

Since the discovery of macroscopic synthetic methods of fullerene C₆₀, a large number of reports have been published on the preparation and characterization of fullerene adducts and derivatives.¹ Due to the highly conjugated low-lying LUMO orbital, C₆₀ is demonstrated to easily undergo electrocyclic reactions such as 1,3-dipolar cycloadditions² and Diels–Alder reactions.³ Among the established reactions, the dipolar cycloaddition of diazoalkanes has attracted particular attention as a result of the interesting reaction features depending on the structures of diazoalkanes.⁴ The primary [3 + 2] addition preferentially occurs at the [6,6] ring conjunct double bond to yield [6,6]-closed pyrazoline adducts.^{4a–c} Subsequent nitrogen-

release leads to [6,5]-open fulleroids and then valence isomerization provides more stable [6,6]-closed methanofullerenes.⁵

Besides the mechanistic study, the quantitative elucidation of the chemical reactivity as well as the physicochemical properties of fullerenes are very important issues in view of the syntheses of modified derivatives, the control of regio-

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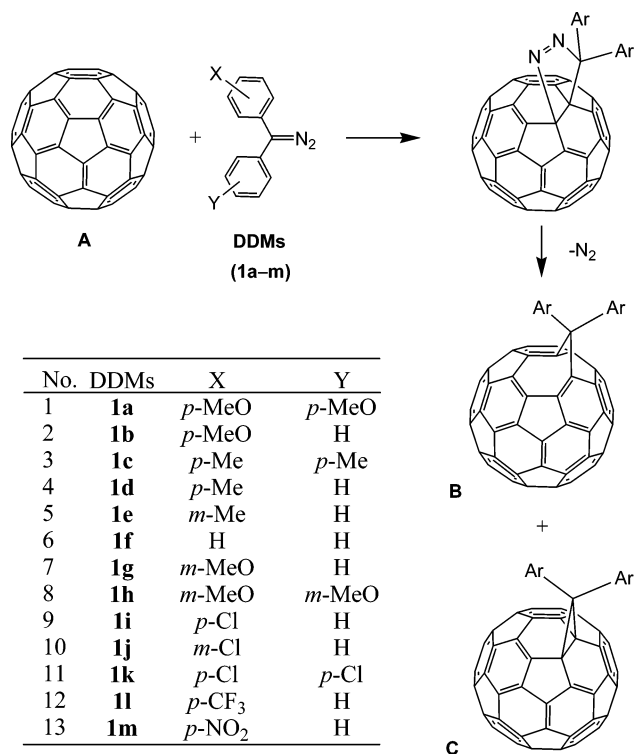
chemical functionalization, and the further development of fullerene chemistry. For example, Haddon et al. reported a comparative study of electron-withdrawing substituents on methanofullerene (C_{61}), correlating the first reduction potential with the Hammett σ_m .⁶ Scorrano et al. tried to quantitatively evaluate the substituent effect of fullerene ring from the pK value of a fullerene based benzoic acid.⁷ However, to the best of our knowledge, a systematic kinetic study of the reaction of C_{60} and higher C_{70} has not yet been reported.^{3b} In addition, the question remains open as to whether the C_{60} is more reactive than C_{70} and on how large the reactivity of C_{60} is as compared with the common acceptor dipolarophiles.

To gain more insight into the chemical reactivity of fullerenes C_{60} and C_{70} , we have investigated the kinetics of 1,3-dipolar cycloaddition of a series of meta- and para-substituted diphenyldiazomethanes (DDMs, **1a–m**) with spherical C_{60} and C_{70} as a model reaction (Scheme 1). We have also compared them with similar additions of DDMs to TCNE, DDQ, and chloranil (CA) to explore the steric and electronic effects of fullerene reactions.

Results and Discussion

Kinetic Measurements. The kinetic measurements were carried out under pseudo-first-order conditions, using a large

SCHEME 1



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excess of DDMs (25–50 equiv) with respect to C_{60} and C_{70} . The progress of the reaction was followed by HPLC, using a Buckeyprep column. The representative HPLC chart obtained for the kinetic solution initially containing C_{60} (1.0×10^{-3} mM) and **1c** (4.0×10^{-2} mM) in toluene at 30 °C on 0.5 h standing was shown along with the time course of the product distributions in Figure 1. There is the buildup of two monoadducts (fulleroid (B) and methanofullerene (C)) and some bisadducts (D) between peaks of **1c** and C_{60} (A). The identity of adduct B as fulleroid is due to the complete thermal isomerization to the methanofullerene C at 160 °C for 15 h in *o*-dichlorobenzene. Monitoring the kinetic reaction by HPLC showed the gradual increase of both B and C accompanied by the first-order decay of C_{60} (A). Similarly, we also observed the formation of several 1:1 and 1:2 adducts in the reaction with C_{70} (for more details see the Supporting Information).⁸ The natural logarithmic plots of the signal intensities of the remaining C_{60} and C_{70} relative

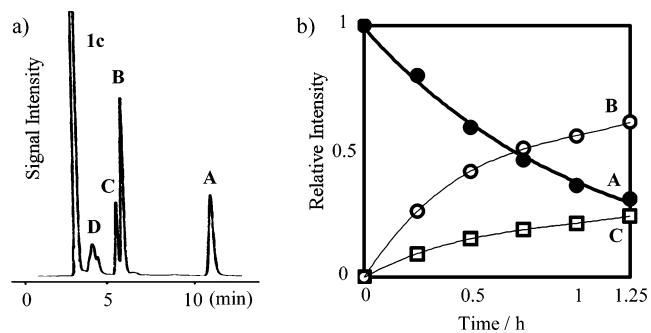


FIGURE 1. (a) Typical HPLC trace of the sample aliquot ($t = 0.5$ h) of the reaction of **1c** and C_{60} with a mixture of toluene/hexane (4/1, v/v). (b) Time course of the reaction of **1c** with C_{60} in toluene at 30 °C. Relative intensity of each component was obtained by dividing its signal intensity by that of the first aliquot C_{60} : C_{60} (A), fulleroid (B), and methanofullerene (C).

TABLE 1. Second-Order Rate Constants ($k/M^{-1} s^{-1}$) for Reaction of DDMs with C_{60} and C_{70} at 30 °C in Toluene

DDMs	$10^2 k^a / M^{-1} s^{-1}$		DDMs	$10^2 k^a / M^{-1} s^{-1}$	
	C_{60}	C_{70}		C_{60}	C_{70}
1a	191	104	1h	7.16	<i>c</i>
1b	49.9	34.7	1i	6.66	3.29
1c	40.6	32.4	1j	3.58	2.17
1d	20.7	12.6	1k	3.13	2.30
1e	12.4	8.29	1l	1.29	0.742
1f^b	11.3	7.83	1m	0.475	0.303
1g	9.76	7.19			

^a Average of at least two measurements. Error limit is $\pm 2\%$. ^b The rate constants ($10^2 k / M^{-1} s^{-1}$) at other temperatures (38, 44, and 50 °C) are 17.9, 23.4, and 31.8 for C_{60} and at 40 and 50 °C they are 13.0 and 23.0 for C_{70} , respectively. ^c Not observed.

to those of the first aliquots ($t = 0$) gave the linear correlation against time more than 70% completion of the reaction. The obtained slope, that is, the pseudo first-order rate constant k_{obs} , was divided by the corrected concentration of DDMs to provide the second-order rate constants k_2 .⁹ The k_2 values thus obtained for various DDMs (**1a–m**) were collected in Table 1.

Kinetic Substituent Effects. A brief survey of Table 1 indicates the two noticeable points: (1) the rates were accelerated by the electron-releasing (donor) substituent of DDMs and (2) C_{60} tended to react with DDMs 1.3–2 times faster than C_{70} .

We first discuss point 1. This rate enhancement can be easily rationalized in view of the typical 1,3-dipolar cycloaddition between DDMs (type I class dipole as characterized by Sustmann¹⁰) and fullerenes (acceptor dipolarophile). Namely, the electron-releasing meta and para substituents lift the HOMO energies of DDMs and hence diminish the energy gap between HOMO (DDMs) and LUMO (fullerenes). This electronic effect leads to the acceleration of rate by the increased energy gain in the transition state according to the simple application of FMO theory to the comparison of reactivity sequences.¹⁰ Thus, the *p*-MeO-substituted **1b** provided ca. 110-fold larger rate constant than *p*-NO₂-substituted **1m** for both C_{60} and C_{70} (Table 1).

To assess the degree to which the fullerene reactions respond to the meta and para substituent changes of DDMs, we applied the free energy relationships for $\log(k/k_0)$, where k_0 refers to the rate constant for the unsubstituted DDM (**1f**). It was found that the two-parameter Yukawa–Tsuno (Y–T) equation¹¹ gave excellent results for both C_{60} and C_{70} reactions (eqs 1 and 2) (for the single parameter treatment with the Hammett σ and the Brown σ^+ scale,¹² see the Supporting Information).

$$\log(k/k_0) = -1.61(\sigma + 0.216\Delta\bar{\sigma}_R^+) + 0.02$$

$$(R^2 = 0.98, n = 13) \text{ for } C_{60} \quad (1)$$

(8) In the case of C_{70} , we observed the formation of several 1:1 and 1:2 adducts by HPLC. We have also confirmed by HPLC and ¹H NMR that the fulleroid thermally rearranges to the corresponding methanofullerene as found for the reaction with bis(4-anisyl)diazomethane (**1a**).

(9) The corrected concentration of DDMs was obtained by subtracting the half amount of C_{60} or C_{70} from the initial one.

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$$\log(k/k_0) = -1.66(\sigma + 0.167\Delta\bar{\sigma}_R^+) + 0.00$$

$$(R^2 = 0.98, n = 12) \text{ for } C_{70} \quad (2)$$

It is easily noted that C_{60} gives a slightly smaller negative ρ value (–1.61) but somewhat larger resonance reaction constant ($r = 0.216$) compared to C_{70} (–1.66 and 0.167, respectively). These smaller negative ρ and positive r values imply that the appearance of positive charge on the diazo-carbon as well as its resonance stabilization is rather small in the rate-determining transition state. This is in harmony with the concerted mechanism of symmetry allowed [$\pi 4_s + \pi 2_s$] cycloaddition¹³ of larger HOMO–LUMO energy difference. The differential reactivity between C_{60} and C_{70} (as to the above point 2) will be discussed in the last section.

A Comparison with TCNE, DDQ, and Chloranil (CA) Reactions. (a) Dependency of Rates on the Meta and Para Substituents. Fundamental knowledge of the chemical reactivity of fullerenes as compared to the common acceptors is very eagerly desired from synthetic and theoretical viewpoints. Fortunately, we have previously investigated the kinetic substituent effects in the 1,3-dipolar cycloaddition of DDMs with some typical acceptors such as TCNE,¹⁴ DDQ,¹⁵ and chloranil (CA).¹⁶ Before describing the kinetic substituent effects of these representative acceptors, we must consider the reaction features of these 1,3-dipolar cycloadditions. TCNE is known to react with DDMs at the electron-deficient central C=C double bond to afford tetracyanocyclopropane derivatives via a rapid nitrogen release from the primary [3 + 2] adduct pyrazolines.¹⁴ On the other hand, due to steric reasons, DDQ and CA react exclusively at the less hindered outer C=O group rather than the inner C=C bond to give very labile 3-oxapyrazolines which quickly lose nitrogen to become the betaine intermediates.^{15,16}

Although the solvents were different from that of the present fullerene reactions (toluene), these reactions exhibited rather more enhanced kinetic substituent effects with larger negative ρ values and raised resonance reaction constants (r), i.e., TCNE ($\rho = -2.67$ for the Brown–Okamoto equation (corresponding to $r = 1.0$ for the Y–T equation by definition),¹⁴ in benzene at 30 °C), DDQ ($\rho = -2.33$ for Y–T equation ($r = 0.47$), in benzene at 30 °C),¹⁵ and CA ($\rho = -1.69$ for Y–T equation ($r = 0.66$), in THF at 30 °C),¹⁶ respectively. Assuming that the substituent effects are not so significantly affected by changing solvents in a narrow range of solvent polarity as represented by Reichardt's E_T values,¹⁷ i.e., toluene ($E_T = 33.9$), benzene (34.3), and THF (37.4), it can be said that the electron withdrawal from the sp² diazo-carbon of DDMs increases in the order of TCNE > DDQ > CA > $C_{70} \geq C_{60}$.

We can more explicitly recognize the relative magnitude of the kinetic substituent effects for each acceptor when the $\log k(\text{acceptor})$ was plotted against the $\log k(C_{60})$ as reference (Figure 2). First noticeable is that a beautiful linear free energy relationship has been found to hold for all acceptors investigated. The regression lines provided the slopes of 2.56 ($R^2 > 0.99$) for TCNE, 1.57 ($R^2 = 0.99$) for DDQ, 1.29 ($R^2 = 0.99$) for

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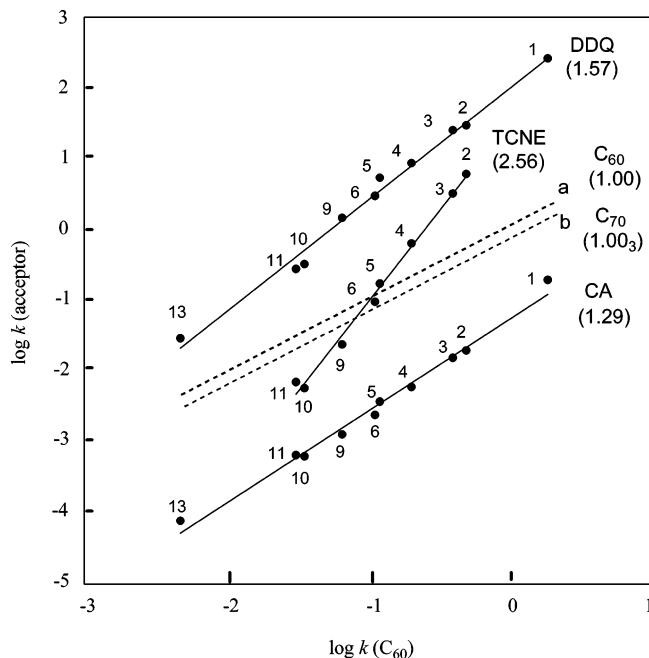


FIGURE 2. Plots of $\log k$ (acceptor) versus $\log k$ (C_{60}) at 30 °C: (1) **1a**, (2) **1b**, (3) **1c**, (4) **1d**, (5) **1e**, (6) **1f**, (7) **1g**, (8) **1h**, (9) **1i**, (10) **1j**, (11) **1k**, (12) **1l**, and (13) **1m**. The solvents are benzene (for DDQ and TCNE), toluene (for C_{60} and C_{70}), and THF (for CA). The broken lines a and b stand for C_{60} and C_{70} , respectively. The values in parentheses are the slopes of the regression lines (unit slope for C_{60}). All the regressions provided good correlation coefficients ($R^2 \geq 0.99$).

CA, and 1.003 ($R^2 > 0.99$) for C_{70} (broken line b), respectively. By definition, the reference C_{60} reaction gives the unit slope through the origin (broken line a). The magnitudes of these slopes refer to the relative sensitivity of each acceptor on the substituent changes of DDMs as compared with reference C_{60} . The steepest TCNE line crossed with the C_{70} and C_{60} lines.

To address these substituent effects, we must consider several factors which affect the electronic state of the central diazo-carbon of DDMs. It is evident that the strong acceptor will significantly withdraw electron from the relevant diphenyl-bearing carbon atom (i.e., charge transfer from DDMs to acceptor) in the transition state. One of the most important criteria for the electron affinity is the reduction potential (E^{red}) or LUMO energy of the acceptor¹⁸ because more positive E^{red} (the more lower LUMO) brings about more enhanced electron withdrawal from the transition state DDMs, thus inducing more development of positive charge on the central diazo-carbon. In addition, the LUMO coefficients at the reaction site of the acceptor play a crucial role in the magnitude of the orbital interaction with the HOMO of DDMs. According to the FMO model, reactions take place preferably in the maximal HOMO-LUMO overlap with the product of (large) \times (large) orbital coefficients than the others.¹⁹ Moreover, the steric bulk of acceptor exerts the some inhibition about performing the ideal orbital interaction with DDMs.

Keeping in mind the above considerations, we will discuss the kinetic substituent effects of fullerenes as compared to those of DDQ, TCNE, and CA. The first reduction potentials (E^{red} vs

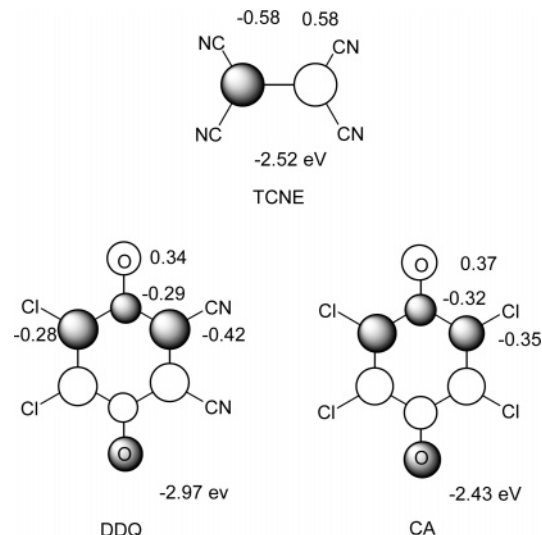


FIGURE 3. LUMO of TCNE, DDQ, and chloranil (CA) by MOPAC PM3 calculation.

SCE) of the acceptors studied increase in the order of DDQ (+0.50 V, CH_3CN)²⁰ > TCNE (+0.24 V, CH_3CN)²¹ > CA (-0.01 V, CH_3CN)²⁰ > C_{70} (-0.41 V, CH_2Cl_2)²² > C_{60} (-0.44 V, CH_2Cl_2).²² Therefore, the smaller negative ρ values for C_{60} and C_{70} can be explained by the weaker electron affinity as well as the smaller LUMO coefficients.²³

By contrast, TCNE exhibited the highest substituent dependency despite a lower E^{red} than DDQ. This discrepancy may be rationalized by the considerably larger LUMO coefficients of TCNE at the central C=C double bond as compared to the DDQ carbonyl function (Figure 3), because the larger LUMO orbital coefficients cause the more pronounced charge transfer from the HOMO of DDMs.

Strangely, however, CA gave the larger resonance reaction constant ($r = 0.66$) than DDQ (0.47), suggesting the occurrence of more enhanced π -electron-donating delocalization by donor substituent. The π -resonance effects are highly dependent on the conformation of adjoining aromatic rings.²⁴ As a consequence, the delicate balance of these crucial factors, i.e., the electron affinity (LUMO energy), the LUMO coefficients, as well as the conformation of the π -resonating aromatic ring, would determine the magnitudes of kinetic substituent effects as depicted in Figure 2.

(b) Dependency of Rates on Solvents. In Figure 2, we can easily grasp the unexpected higher reactivity of C_{60} and C_{70} as

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(23) For instance, theoretical calculations of the molecular orbitals of C_{60} show that the lowest LUMO (t_{1u} -symmetry) and the LUMO+1 (t_{1g} -symmetry) are triply degenerated and the orbitals possessing the high coefficients are distributed at the multisites of the spherical surface of C_{60} ; see: (a) Reference 1a. (b) Bühl, M.; Hirsch, A. *Chem. Rev.* **2001**, *101*, 1153–1183. (c) Hirsch, A.; Chen, Z.; Jiao, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3915–3917.

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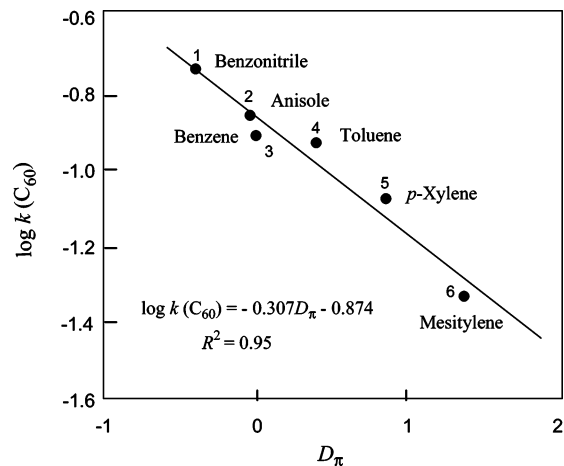
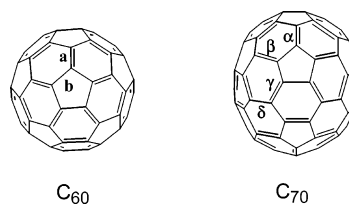
TABLE 2. Second-Order Rate Constants ($k/M^{-1} s^{-1}$) for Reaction of DDM (**1f**) with C_{60} in Various Solvents at 30 °C

solvent	$10^2 k/M^{-1} s^{-1}$	D_π^a	E_T^b
1. benzonitrile	17.8	-0.398	41.5
2. anisole	13.5	-0.043	37.1
3. benzene	12.0	0.000	34.3
4. toluene	11.5	0.394	33.9
5. <i>p</i> -xylene	8.23	0.846	33.1
6. mesitylene	4.60	1.36	32.9

^a Solvent soft basicity parameter, see ref 25a. The D_π values for anisole, *p*-xylene, and mesitylene were newly obtained according to ref 25a.
^b Solvent polarity parameter, see ref 17.

compared to that of TCNE and CA, although the reaction solvents are different from each other, i.e., C_{60} and C_{70} (toluene), CA (THF), TCNE, and DDQ (benzene). Strictly speaking, we must compare the kinetic results which were obtained under the same conditions since the solvents effects are often so noticeable in the chemical reactions.^{17b} Moreover, it is apparent that the acceptor molecule suffers specific solvation, so-called electron-pair donor/electron-pair acceptor (EPD/EPA) interaction.²⁵ When compared in the same reaction conditions at 30 °C in solvent “toluene”, the reaction of C_{60} with unsubstituted DDM (**1f**) (point number 6 in Figure 2) was found to be ca. 3 and 70 times faster than those of TCNE^{25a} and CA,²⁶ respectively, but only 9 times slower than the strongest acceptor DDQ.¹⁵ Here, it is interesting to know the solvent dependency of the rate of C_{60} because the π -donor solvents also seem to play some role in the fullerene reactions. In fact, the rates for the parent reaction of C_{60} with DDM (**1f**) were apt to moderately decrease with the increase of π -electron donating ability of the solvents (Table 2). The obtained k_2 was decreased 4 times by changing solvent from the less basic benzonitrile to the highly basic mesitylene as represented by the solvent soft basicity parameter D_π .^{25a} However, there is no appreciable relationship between the rates and the solvent polarity (E_T). The plots of $\log k$ versus D_π gave a fairly good regression equation ($R^2 = 0.95$) as shown in Figure 4. The negative slope (m) implies that the π -donor aromatic solvents predominantly stabilize the ground-state fullerenes, retarding the reaction. The C_{60} reaction ($m = -0.307$) provided a more gentle slope than the DDQ (-1.14), TCNE (-1.00 by definition), and CA reactions (-0.598).²⁷ Here it is noteworthy that these m values are correlated with the above-mentioned E^{red} of the relevant acceptors, though no corrections of E^{red} were made for the solvent change; $m = -0.933E^{\text{red}} - 0.693$ ($R^2 = 0.96$) (for the plots, see the Supporting Information). This equation proves that the susceptibility of C_{60} to the solvent soft π -basicity increases with the increase of E^{red} .

Factors Influencing the Reactivity of Fullerenes. As described above, fullerenes exhibited the unexpected higher reactivity despite of the poor electron affinity compared with TCNE and CA. This may be attributed to two determining factors: (1) the strain due to pyramidalization of the sp^2 C-atoms in the spherical structures of fullerenes²⁸ and (2) the short [6,6] bonds with larger π -bond orders and higher π -density.²⁹ The magnitude of deviation from the sp^2 planarity is related to the

**FIGURE 4.** Plots of $\log k(C_{60})$ at 30 °C versus solvent soft basicity parameter D_π .**FIGURE 5.** C_{60} : [6,6] bond (a) and [6,5] bond (b). C_{70} : Four types of [6,6] bonds (α – δ).

strain energy at the individual carbon atoms in fullerenes and represented as the useful index of pyramidalization angle (θ_p).²⁸ The major driving force for addition reactions to fullerenes is the resulting relief of strain energy accompanied by rehybridization ($sp^2 \rightarrow sp^3$).^{28a}

As seen in Figure 5, the C_{60} (I_h symmetry) has a single set of equivalent atoms with θ_p ($=11.64^\circ$) regardless of the bond type, [6,6] and [6,5] bond (types a and b).^{28a} This strained angle introduces a large strain energy into C_{60} , which is estimated to be ca. 8 kcal mol⁻¹ per carbon. The [6,6] bond (1.401 Å) is considerably shorter than the [6,5] bond (1.458) and thereby the larger π -bond order is responsible for the exclusive additions at the [6,6] bond as found for the various addition reactions of C_{60} .^{2–4} In recent years, several workers have performed the theoretical investigation on the mechanism and regioselectivity of these cycloadditions with typical dipoles, representing the total agreement with the experimental observations.³⁰

On the other hand, C_{70} (D_{5h} symmetry) has 8 types of chemically different C–C bonds, half of which are [6,6] bonds (types α – δ).^{3b} Among the [6,6] bonds, the most reactive bonds (type α) have slightly larger angles ($\theta_p = 11.91^\circ$ and 11.93° for the two conjunct carbons) than that of C_{60} .^{3b} They scatter at the 10 apical positions in the pole sites (Figure 5). The second reactive bonds (type β) possessing fairly reduced θ_p ($=10.57^\circ$ for both conjunct carbons) and the shortest bond length are

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located at the 10 hexagon sides conjugated with the above type α bonds. Other [6,6] bonds (γ and δ) which are located at the equatorial belt regions are less reactive because of the more reduced strain as well as the longer bond character. Indeed, the addition reactions of C_{70} proceed via the preferential attack at the type α bond³¹ as found for the osmylation³² and 1,3-dipolar cycloaddition of CH_2CN_2 .^{4a,33} For instance, in the addition of diazomethane, the reactivity ratio of 13:2 for type α :type β bond was deduced from the product ratio of the corresponding primary adduct pyrazolines.^{4a} Thus, it is likely that ca. 90% of the rate may be attributed to the attack at the type α bond and the rest to type β attack. Assuming that DDMs also attack C_{70} with a similar site-selectivity, we could imagine that the 1.5 times larger reactivity of C_{60} relative to C_{70} is related to the excess total numbers (30) of the reactive [6,6] bonds (type a) in C_{60} than the less abundant type α bonds (10) in C_{70} . Based on this statistical reasons, it is interesting to note that the intrinsic reactivity per reactive [6,6] bond is ca. 2 times higher for C_{70} than for C_{60} . However, the possibility that the inherent higher reactivity of C_{70} with the slightly lower LUMO is reversed by the basic solvation by toluene could not be thoroughly ruled out by considering the above-mentioned solvent effects.

More interestingly, Duran et al. theoretically analyzed the Diels–Alder (DA) reaction of butadiene with C_{60} and C_{70} and predicted slightly larger reactivity of C_{70} than C_{60} in the gas phase.^{3b} By contrast, they obtained the reverse reactivity order in toluene solution like the present case. This prediction is consistent with an ca. 7 times enhanced rate for C_{60} than C_{70} in the DA reaction with cyclopentadiene at 20 °C in toluene as reported by Pang and Wilson.^{3a} The higher reactivity of C_{60} was rationalized on the basis of the Arrhenius data which were very different between C_{60} and C_{70} . The activation energy (E_a) of C_{60} was by far smaller than half that of C_{70} , whereas C_{70} recovered the handicap with a 2.3 times larger logarithmic frequency factor A . However, as seen in Table 1, the present kinetic data for the reaction of DDM (**1f**) with fullerenes in various temperatures exhibited no essential difference in the activation parameters, i.e., $\Delta H^\ddagger = 39.1$ and 40.1 kJ mol⁻¹ and $\Delta S^\ddagger = -134$ and -134 J K⁻¹ mol⁻¹ for C_{60} and C_{70} , respectively. Our results suggest that the 1,3-dipolar cycloaddition of DDM with C_{60} and C_{70} proceeds through a very similar pathway on the potential energy surface. Current efforts are directed toward the kinetics in the secondary addition of DDMs to these primary products (fulleroids and methanofullerenes) to elucidate the steric and electronic factors which control the reactivity of fullerene derivatives. We also intend to clarify the regioselective reactivity of the four types of [6,6] bonds of C_{70} .

Conclusions

Kinetics of model 1,3-dipolar cycloaddition of a series of meta- and para-substituted diphenyldiazomethanes (DDMs) with fullerenes C_{60} and C_{70} have been investigated at 30 °C in toluene in comparison with similar dipolar addition with TCNE, DDQ, and chloranil (CA). It was found that C_{60} is ca. 1.5 times more reactive than C_{70} . The $\log k/k_0$ values were well correlated by the Yukawa–Tsuno (Y–T) equation with relatively smaller

negative ρ values (-1.6 and -1.7) and diminished resonance reaction constants ($r = 0.22$ and 0.17), compared with the corresponding reactions with stronger acceptors TCNE, DDQ, and CA. The plots of $\log k(\text{acceptor})$ versus $\log k(C_{60})$ as reference also provided the excellent linear free energy relationships and the magnitudes of slopes increased in the order TCNE > DDQ > CA > $C_{70} \geq C_{60}$. The poor substituent dependency of C_{60} and C_{70} can be rationalized by the considerably reduced electron affinity of fullerenes compared with the strong acceptors. On the other hand, the relative reactivity of these acceptors toward the parent unsubstituted DDM increased in the order DDQ > $C_{60} \geq C_{70}$ > TCNE > CA. The unexpected higher reactivity of fullerenes can be inferred by the inherently strained pyramidalization of sp² C-atoms, which strongly assists the additions leading to the relief of strain. The kinetic solvent effects elucidated the ground state stabilization of fullerenes especially by the π -basic donor solvents as represented by the good linear free energy relationship with the solvent basicity parameter D_π . Consequently, the useful information on the chemical reactivity of fullerenes will provide beneficial insight into the physicochemical understanding of reactivity as well as further development of fullerene chemistry.

Experimental Section

Materials. All diphenyldiazomethanes (DDMs) were prepared just before use by oxidation of the corresponding hydrazones with yellow mercury oxide, according to the literature procedure. The solid DDMs (**1a–d**, **1f**, **1i**, **1k**, and **1m**) were purified by recrystallization from a hexanes–ether mixture. The melting points were in accordance with the literature values.¹⁴ The oily DDMs (**1e**, **1g**, **1h**, **1j**, and **1l**) were assessed by HPLC and NMR and found not to be contaminated by the possible azines, carbene dimmers, and benzophenones, as well as the unreacted hydrazones. The C_{60} and a mixture with C_{70} were purchased from Tokyo Kasei Kogyo Co., Ltd. The C_{70} was separated from C_{60} by a preparative HPLC with a Buckeyprep column (20 mm \times 250 mm). Toluene (predried for the synthetic procedure) was commercial and was used without further purification. All other solvents were purified according to the usual manner.³⁴

Kinetic Procedure. For the sake of simplicity, kinetic reaction was carried out in first-order conditions, using a large excess of DDMs (25–50 equiv) with respect to C_{60} and C_{70} (1×10^{-3} mM). Thus, a toluene solution (1 mL) of the excess DDMs was rapidly introduced into a screw-capped test tube containing a 1 mL toluene solution of C_{60} (1×10^{-3} mM), which is preheated at 30 °C in a thermostated bath. The reaction solution was heated for a requisite time at 30 °C and a constant aliquot (10 μ L) was removed by a microsyringe at regular time intervals for HPLC analysis as described below. The progress of reactions was followed by monitoring the decrease of the absorption peak intensity of C_{60} with a HPLC instrument equipped with a UV operating at 280 nm, a calculating integrator, and an analytical Buckey-prep column (4.6 mm \times 250 mm). A hexane–toluene mixture ($\sim 30\%$ v/v) was used as a mobile phase.

Supporting Information Available: Five figures for the typical HPLC trace of reaction of **1a** with C_{70} as well as the HPLC charts showing the thermal rearrangement of the fulleroid to the methanofullerene, ¹H NMR charts exhibiting the thermal rearrangement of fulleroid to the methanofullerene, plots of $\log k/k_0$ vs Hammett σ and Brown σ^+ for C_{60} and C_{70} , respectively, and then plots of solvent dependency on the D_π parameter vs the reduction potential E^{red} of acceptors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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