Ionization and electron excitation of \( \text{C}_{60} \) in a carbon nanotube: A variable temperature/voltage transmission electron microscopic study

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There is increasing attention to chemical applications of transmission electron microscopy, which is often plagued by radiation damage. The damage in organic matter predominantly occurs via radiolysis. Although radiolysis is highly important, previous studies on radiolysis have largely been descriptive and qualitative, lacking in such fundamental information as the product structure, the influence of the energy of the electrons, and the reaction kinetics. We need a chemically well-defined system to obtain such data and have chosen as a model a variable-temperature and variable-voltage (VT/VV) study of the \([2+2]\) dimerization of a van der Waals dimer \([60]\) fullerene \((\text{C}_{60})\) to \(\text{C}_{120}\) in a carbon nanotube (CNT), as studied for several hundred individual reaction events at atomic resolution. We report here the identification of five reaction pathways that serve as mechanistic models of radiolysis damage. Two of them occur via a radical cation of the specimen generated by specimen ionization, and three involve singlet or triplet excited states of the specimen, as initiated by electron excitation of the CNT, followed by energy transfer to the specimen. The \([2+2]\) product was identified by measuring the distance between the two \(\text{C}_{60}\) moieties, and the mechanisms were distinguished by the pre-exponential factor and the Arrhenius activation energy—the standard protocol of chemical kinetic studies. The results illustrate the importance of VT/VV kinetic analysis in the studies of radiation damage and show that chemical ionization and electron excitation are inseparable, but different, mechanisms of radiation damage, which has so far been classified loosely under the single term “ionization.”

excited-state chemistry | radiation chemistry | radical cation | fullerene | transmission electron microscopy

Since the time of the Knoll/Ruska invention of transmission electron microscopy (TEM) (1), electron microscopy has suffered from information loss during observation often ascribed to the structural changes of a specimen into a different substance, known as radiation damage (2). As summarized recently by Egerton (3), the electron-beam (e-beam) damage in organic matter predominantly occurs via processes triggered by ionization (radiolysis). Although radiolysis is highly important, studies on radiolysis have largely been descriptive and qualitative because of the complexity of the process and the difficulty in quantifying the changes under variable-temperature and variable-voltage (VT/VV) conditions. The first step of the process involves electron-impact ionization (EII), which removes an electron to form a radical cation (RC) of the specimen, and also electron-impact excitation (EIE), where the electron does not fly away to the vacuum, but stays in a higher antibonding state in the system. The processes were recently studied in depth for the first time by a thorough quantum chemical study (4). There has been, however, a paucity of experimental mechanistic information—that is, how a specimen is transformed to what product with what level of activation energy and frequency at what acceleration voltage. Single molecules encapsulated in a carbon nanotube (CNT) have often been observed either stably or undergoing well-defined chemical transformations (5–9), and it is primarily because the damage due to secondary electrons is minimal (10). Drawing an analogous specimen stabilization by a thin metallic coating or deposition on a conductive indium tin oxide substrate in scanning electron microscopy (SEM) (11), we can consider that the electron-rich CNT interacts with the specimen molecules and protects them from ionization by filling in the electron vacancy in the RC. In light of the recent characterization of singlet and triplet excitons of CNTs (Fig. 1A) (12), we can also consider that the CNT exciton would excite a molecule in the CNT via energy transfer (ENT) (Fig. 2A) (13, 14). Electron excitation of graphene under TEM conditions has also been suggested recently (15, 16).

We report here the VT/VV kinetic study of the dimerization of a van der Waals (vdW) dimer \([60]\) fullerene \((\text{C}_{60})\) to \(\text{C}_{120}\) in a CNT (17–19), in which we found five

Significance

The destruction of specimen molecules by an electron beam (e-beam) is either beneficial, as in mass spectrometry capitalizing on ion formation, or deleterious, as in electron microscopy. In the latter application, the e-beam not only produces the specimen image, but also causes information loss upon prolonged irradiation. However, the atomistic mechanism of such loss has been unclear. Performing single-molecule kinetic analysis of \(\text{C}_{60}\) dimerization in a carbon nanotube (CNT) under variable-temperature/voltage conditions, we identified three reactive species—that is, radical cation, singlet, and triplet excited states—reacting competitively as the voltage and the properties of the CNT were changed. The key enabler was in situ continuous recording of the whole reaction process, suggesting an upcoming new era of “cinematic chemistry.”

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competing reaction pathways that serve as model pathways of radiolysis damage (Fig. 1 B–F). We found a marked influence of the temperature, the acceleration voltage, and the properties of the CNT—pristine CNT (prCNT), oxidized CNT (oxCNT), or damaged CNT (dmCNT) (Fig. 2 B). They have been distinguished by the pre-exponential factor (PEF) and the Arrhenius activation energy (E_a). Singlet (S_1) and triplet (T_1) species generated by ENT from a CNT exciton account for frequently occurring reactions (Fig. 1 B and C) (3). The triplet reaction also occurs when we use an oxCNT (Fig. 1 D), which is known to form a triplet exciton. Electrons of 60 keV in energy cannot energize prCNT to either the singlet or the triplet state, but instead directly ionize C_60 into the RC. The RC is then reduced by the CNT to a mixture of S_1 and T_1 states (Fig. 1 E). This process illustrates how prCNT protects the specimen from radiolysis by “grounding” (Fig. 2 C) and accounts for the stability of a variety of molecules having low-lying highest-occupied molecular orbitals, such as saturated hydrocarbons (20), amides (21), alcohols (22), and inorganic salts encapsulated in a CNT (23, 24). We observed the RC when the reaction was performed in dmCNT (Fig. 1 F). The VT/VV behavior of the kinetics agrees with the competitive occurrence of electron excitation and ionization, but not with the atomic displacement damage mechanism, which is the major cause of radiation damage in conductive inorganic materials (25).

Light transfers its energy to a zero-dimensional (0D) material via an electric dipole transition (EDT) mechanism with conservation of spin-angular momentum (30). CNT resembles 0D materials due to van Hove singularities (Fig. 1 A) (31), and we envisaged that the CNT exciton transfers energy to C_60 encapsulated in CNT (Fig. 2 A). Note that the thermally forbidden [2 + 2] dimerization of vdW (C_60)_2 does not take place at temperature < 800 K (32). The reaction commences upon photo-irradiation of C_60 film or solid (33, 34) and also occurs upon electron irradiation (Fig. 3 A, box). Further irradiation converts the initially formed [2 + 2] dimer eventually to a short CNT (18) via retro [2 + 2] cycloaddition and a series of Stone–Wales rearrangements (Fig. 3 A) (35).

In 2011, C_60 dimerization in CNTs was reported to take place even with 20-keV irradiation, although it then requires a 100-times-larger electron dose that at 80 kV (36). The 20-keV energy is far lower than the threshold voltage of carbon atom displacement (CAD; knock-on displacement), and hence CAD is an unlikely mechanism of the C_60 dimerization. A 60-keV e-beam was recently reported to cause reactions of C_60 sandwiched between two graphene sheets—loss of one carbon atom to form a C_118 (quasi) dimer via C_59 (37). This may suggest a difference between a one-dimensional (1D) CNT and gapless two-dimensional (2D) graphene that lacks van Hove singularities (Fig. 1 A). This is briefly examined in the present study.

**Results**

Variable-temperature single-molecule atomic-resolution time-resolved electron microscopic (VT-SMART-EM) imaging is an emerging experimental tool for the study of kinetics and thermodynamics of individual chemical events (19, 22, 38), and it has provided direct experimental proof of the Rice–Ramsperger–Kassel–Marcus theory (39). In this study, we
monitored several hundred individual events of the [2 + 2] reaction under VT/VV conditions at 103 to 493 K and 60 to 120 keV (10, 19). Following the reaction conditions developed previously (19), we encapsulated the fullerene molecule in a bundle of prCNTs, oxCNTs, or dmCNTs, 1.3 to 1.4 nm in diameter (40), by heating them together at 823 K for 15 h in vacuo. A specimen was deposited on a TEM grid, and the time evolution of the [2 + 2] cycloaddition of a (C_{60})2@CNT was visually monitored under e-beam irradiation at 120, 100, 80, and 60 kV, with a constant electron dose rate (EDR) of 3.1 \times 10^5 e^{-} \text{nm}^{-2} \text{s}^{-1} for 120 kV and 5.0 \times 10^6 e^{-} \text{nm}^{-2} \text{s}^{-1} for 60 to 100 kV throughout this study. We examined frame rate ranging from 533 frames per second (fps) to 2 fps (40) and employed the 2-fps rate because the higher frame rates do not reduce the magnitude of error that originates largely from the inhomogeneity of the specimens. Note that the reaction rate per electron measured in the present work is not affected by the variation of EDR as previously reported, indicating that the observed reaction events occur independently (19).

The cycloaddition event was characterized by the change in intermolecular distance from 1.00 nm for the vdW dimer to 0.90 nm for the cycloadduct (Fig. 3B), and the Ea and PEF were determined (19). The [2 + 2] cycloadduct features a strained cyclobutane ring in the middle and reverts to two molecules of C_{60} upon heating at >500 K, thus providing compelling chemical evidence that the adduct is the C_{120} cycloadduct (Fig. 3A).

**Voltage-Dependent Singlet and Triplet Dimerization of a (C_{60})2@prCNT.** Unlike photo-excitation of \(\pi\)-conjugated molecules, in which the photo energy is efficiently transferred to the molecule via an EDT mechanism, electron excitation of a molecule by momentum transfer from an e-beam is very inefficient. To assess how inefficient it would be, and to know the consequence of poor efficiency, we performed the kinetic analysis at an acceleration voltage decreasing stepwise from 120 keV to 60 keV.
In Fig. 4, we show the kinetics data of the dimerization in prCNT at 60 to 120 keV at 443 to 493 K. The raw data at 443 K are shown in Fig. 4A, where we plot the number of dimerization events observed at intervals of $8.0 \times 10^6$ e$^-$/C$_0$/C$_1$nm$^2$/C$_0^2$ irradiation against the total electron dose (TED) up to $3.0 \times 10^8$ e$^-$/C$_1$/nm$^2$/C$_0^2$ (for 60 s). After in situ monitoring of the reactions of 39 to 55 C$_{60}$ dimerization events at acceleration voltages of 120 (black), 100 (red), 80 (blue), and 60 kV (green; Fig. 4A), we observed three features. First, each reaction event takes place stochastically (41). Second, the occurrence of the events follows the first-order kinetics shown in Fig. 4B and C, where the $1 - P$ and ln$(1 - P)$ values are plotted against TED ($P$ = normalized conversion of C$_{60}$). Third, we find three different kinetic profiles (Fig. 4E).

The rate constants ($k$) at 100 kV are summarized in Fig. 4D. The error is arguably large for several reasons. The CNT is a mixture of entities having different chirality indexes (i.e., the diameters) (42) and different physicochemical environments. In addition, molecular packing in CNTs changes as the dimerization reaction progresses.

Using the rate constants $k$ obtained at five temperatures, we plotted the Arrhenius plot to obtain the activation energy ($E_a$) slope and PEF ($y$-intercept) (Fig. 4E). The slope of the 120- and 100-kV reactions (black and red) was the steepest, and the $E_a$ values at 120 and 100 kV are nearly identical, $33.5 \pm 6.8$ and $32.9 \pm 6.0$ kJ/mol$^{-1}$, respectively, indicating the same reaction mechanism. As one would expect, the 120-kV reaction [PEF = $3.9 \times 10^{-5}$ (e$^-$)$^{-1}$nm$^2$] occurs more frequently than the 100-kV reaction [PEF = $5.9 \times 10^{-5}$ (e$^-$)$^{-1}$nm$^2$].

The slope of the Arrhenius plot of the 80-kV reaction (blue) is half as steep as those of the 120- and 100-kV reactions and the $E_a$ values of $13.4 \pm 3.6$ kJ/mol$^{-1}$, indicating that the reactive species is more reactive than the one at 120- and 100-kV. The PEF value of $1.2 \times 10^{-7}$ (e$^-$)$^{-1}$nm$^2$ is far smaller than those at 120 and 100 kV, indicating that the reaction occurs 1,000 times less frequently. Overall, the reaction at 80 kV is slower than at 120 and 100 kV (Fig. 4B).

The reaction at 60 kV was markedly slower at $\sim 400$ K than the reaction at 100 to 120 kV (Fig. 4B and SI Appendix, Fig. S3). The Arrhenius plot (green, Fig. 4E) deviates from linearity, indicating that the mechanism changes as the temperature changes. We averaged the data over 443 K and 493 K and obtained an $E_a$ value of $20.8 \pm 6.1$ kJ/mol$^{-1}$ and PEF = $3.7 \times 10^{-7}$ (e$^-$)$^{-1}$nm$^2$. These values fall between those at 100 to 120 kV and at 80 kV.

The Arrhenius plot indicated the formation of one type of reactive species at 100 to 120 kV, another at 80 kV, and probably a mixture of the two at 60 kV. We assign the species to the S$_1$ state, the T$_1$ state, and a mixture of the two, respectively. While the details will be discussed below, we point out here
that EIE with high-energy e-beam (e.g., 120 keV) occurs with conservation of spin-angular momentum (30) and hence generates the singlet exciton of CNT and singlet excited state of C60. Second, we also note that the Ea and PEF values at 80 kV are essentially the same as those in the reaction in oxCNT, which can only generate the T1 species by acting as a triplet sensitizer (see below). In Fig. 4, we show a schematic orbital diagram of the concerted singlet cycloaddition, which is a reference standard of the [2 + 2] cycloaddition governed by the Woodward–Hoffmann orbital symmetry rule.

**Triplet Dimerization of a (C60)2@oxCNT.** The oxCNT (Fig. 2B), prepared by using KMnO4 oxidation of a CNT (43), has both the π- and σ-carbon skeletons destroyed by chemical oxidation, as demonstrated by infrared (IR) absorption (due to benzophenone-like groups) (44). It is reported to be a triplet sensitizer in solution, as efficient as benzophenone, and has a triplet energy lower than ~2.5 eV (45), and hence we expect that oxCNT will generate the T1 C60 species. We encapsulated C60 in oxCNT and studied 30 to 52 vdW C60 dimers [(C60)2@oxCNT].

The time course of the dimerization events at 120 kV, with a constant EDR of 3.1 × 10⁶ e⁻·nm⁻²·s⁻¹, is shown in Fig. 5A and the frequency integrated over time in Fig. 5B. The semilogarithmic plot in Fig. 5C gives the reaction rates at temperatures between 378 and 453 K, and the Arrhenius plot gives Ea and PEF values, both of which are small in magnitude (Fig. 5D). These values ascribable to T1 are similar to the data found in a prCNT at 80 kV (blue line, Fig. 4E). In Fig. 5E, we show at a schematic orbital interaction in the triplet cycloaddition reaction.

**RC Dimerization of a (C60)2@dmCNT.** C60 dimerization at 103 to 203 K occurred with an induction period (Fig. 6C) (19),
during which the π-conjugation of the CNTs was destroyed, as seen in Fig. 6A and B (46). After the induction period, a steady first-order reaction took place. We measured the reaction rate and obtained $E_a = 1.7 \pm 0.6 \text{kJ/mol}$ and PEF = $1.3 \times 10^7$ (e–)–1 nm2 (Fig. 6D).

The $E_a$ value close to zero suggests an RC, which is formed by ionization and is expected to be extremely reactive (Fig. 6E).

Ionization is the standard damage mechanism of radiolysis (3), and our observation shows that ionization of C60 does occur, when the π-conjugation in the surrounding CNT is destroyed and has lost its grounding function (Fig. 2C).

Discussion

Table 1 summarizes the $E_a$ and PEF data in prCNTs, oxCNTs, and dmCNTs of the five reaction types (Fig. 1B–F). The kinetic profiles are color-coded in black, blue, green, and purple. We consider that the path with $E_a$ values of 32.9 to 33.5 ± 6 kJ·mol–1 in Table 1 (black) took place via $S_1$, first because a high-energy e-beam excites CNT with conservation of spin-angular momentum (30) and second because the values compare favorably (within experimental error) with an $E_a$ value of 28 kJ·mol–1 (a value calculated from figure 5 of ref. 47) reported theoretically for $S_1$ [2 + 2] cycloaddition in gas phase (47). We assign the $E_a$ values of 31 to 35 kJ·mol–1 in Table 1 (blue), as obtained for the oxCNT to the $T_1$ pathway (48) because an oxCNT is an effective triplet sensitizer due to aromatic ketone residues that accelerate relaxation of singlet to triplet (49). The low values of $E_a$ agree with the biradical character of the $T_1$ excited state of C60. Similarly, we assign $T_1$ to the 80-keV experiment in a prCNT (Table 1) because the kinetic data agree with those for an oxCNT in Table 1 (blue). The value of 20.8 kJ·mol–1 at 60 keV in Table 1 (green) coincides with a value of 23 kJ·mol–1 determined for photodimerization, which likely reflects the consequence of ISC from singlet to triplet in a 1:3 ratio (50).

The SMART-EM study on the electron-impact-promoted [2 + 2] cycloaddition mediated by CNTs (Fig. 7) is unique in that we can study in situ the individual reaction events one by one as they take place. The first stage is a fast EIE reaction, characterized by the PEF data. The second stage is a slow, thermally driven reaction of excited C60 going across an energy barrier with a frequency of $\exp(-E_a/RT)$. We determined the kinetic parameters separately for the two steps by visually monitoring the individual events of the forward cycloaddition of vdW complexes, which excludes the contribution of cycloreversion and reversible collisions from the kinetic data analysis. The ln(PEF) values represent ln($k$) at $T = \infty$, and they vary widely between −7.9 and −16.4 [PEF = $3.9 \times 10^{-4}$ to $1.2 \times 10^{-7}$ (e–)–1 nm2]. They are also extremely low in absolute magnitude, indicating that a large number of electrons ($1.0 \times 10^3$ to $3.0 \times 10^6$ electrons) are required to form one excited or ionized C60 molecule (area of 0.396 nm2) that produces the dimer. The $E_a$ values (slope) reflect the reactivity of Fig. 5. Kinetic study of C60 dimerization in an oxCNT. (A) Occurrence of stochastic reaction events of C60 dimerization inside oxCNTs at 120 kV integrated over every $8.0 \times 10^6$ e–·nm–1 at 438 K for a (C60)2@oxCNT plotted against TED (SI Appendix, Table S4 and Figs. S4 and S5). (B) Reaction progress of C60 dimerization inside oxCNTs at 120 kV. (C) First-order kinetics of C60 dimerization inside oxCNTs at 120 kV. (D) Arrhenius plot of C60 dimerization inside oxCNTs at 80 to 120 kV. (E) Mechanistic sketch of the $T_1$ reaction.
these species in the thermal dimerization reaction (Fig. 7, second step).

To describe the efficiency of the reaction, we borrow the concept of external quantum efficiency (EQE) used to evaluate the efficiency of photovoltaic devices—the ratio of the number of electrons and holes generated by a device to the number of incident photons shining on the device from outside. Similarly, we can define the EQE based on the number of dimers formed relative to the TED shining on the CNT. The EQE values of the S1 reaction in a prCNT and the T1 reaction in an oxCNT at 120 kV are \(9.8 \times 10^7/C_0^4\) and \(2.1 \times 10^6/C_0^6\), respectively, indicating that the latter is nearly 1,000 times less efficient because of the infrequent formation of the triplet exciton of the CNT. The very low value of the energy-attenuation factor (\(\sim 10^5/C_0^4\); from \(\sim 100\) keV to \(\sim 2\) eV) reflects the lack of a mechanism for efficient ENT from the e-beam to the CNT and the loss of energy to phonon vibration of the CNT and physicochemical processes.

The Arrhenius plots for the four representative reactions in Fig. 8 summarize the present finding. In accordance with the accepted mechanism of radiation damage, the ionization pathway operates in dmCNT (purple). In prCNT encapsulating C60 (>300 K), the ionization is suppressed, and much faster excited-state pathways dominate when the energy of the e-beam is >80 keV (black and blue). When the e-beam energy is 60 keV, it does not excite the CNT and hence C60. The S1 species forms in the reaction of C60@prCNT at 120 kV (black) that took place most frequently [the largest ln(PEF) value of \(-7.9\)]. The other three pathways via EIE or EII occurred \(\sim 500\) times less frequently. Extremely reactive RC (purple) reacted with near-zero \(E_a\) and very small ln(PEF) = \(-15.9\) (51). We estimate the ln(PEF) of the CAD of C60 to be approximately \(-15\) to \(-27\), shown as a gray band in Fig. 8, based on the ln(PEF) of RC and the reported frequency difference of \(\sim 10^7\) between CAD and radiolysis of organic matters (52). Because CAD is temperature-independent (37), we estimate ln(\(\delta\)) to be approximately \(-25\) to \(-27\). Thus, the carbon loss of C60 would occur \(\sim 10^{-5}\) times more slowly than that of the excited-state reactions. We thus expect CAD to become noticeable only after irradiation with TED of \(10^9\) to \(10^{11}\), a dose 100 times greater than that used for SMART-EM imaging. The probability of the atom displacement depends on the elastic-scattering cross-section, which decreases as the atomic number decreases.

### Table 1. \(E_a\) and PEF values obtained from the Arrhenius plot of the C60 dimerization events

| e-beam, keV | \(E_a\), kJ·mol\(^{-1}\) | ln(PEF) | PEF, (e-)^{−1}·nm\(^2\) | Path |
|------------|-----------------|--------|-----------------|-----|
| \((C_60)_2\)@prCNT | | | | |
| 120 | 33.5 \(\pm\) 6.8 | \(-7.9 \pm 1.8\) | \(3.9 \times 10^{-4}\) | S1 |
| 100 | 32.9 \(\pm\) 6.0 | \(-9.7 \pm 1.6\) | \(5.9 \times 10^{-5}\) | S1 |
| 80 | 13.4 \(\pm\) 3.6 | \(-15.9 \pm 1.0\) | \(1.2 \times 10^{−2}\) | T1 |
| 60 | 20.8 \(\pm\) 6.1 | \(-14.8 \pm 1.8\) | \(3.7 \times 10^{−7}\) | S1/T1 |
| \((C_60)_2\)@oxCNT | | | | |
| 120 | 11.4 \(\pm\) 4.5 | \(-14.0 \pm 1.3\) | \(8.3 \times 10^{−2}\) | T1 |
| 100 | 15.5 \(\pm\) 5.6 | \(-13.9 \pm 1.9\) | \(9.3 \times 10^{−2}\) | T1 |
| 80 | 15.5 \(\pm\) 6.2 | \(-14.8 \pm 1.8\) | \(3.9 \times 10^{−7}\) | T1 |
| \((C_60)_2\)@dmCNT | | | | |
| 120 | 1.7 \(\pm\) 0.6 | \(-15.9 \pm 0.5\) | \(1.3 \times 10^{−7}\) | RC |

Color coding is according to the reactive species. Colors correspond to the reactive species shown in Figure 8.
Putting together the above experimental data and the literature information, we suggest, in Fig. 9, the two mechanistic possibilities of radiolysis/ionization of the specimen (Fig. 9A) and excitation (Fig. 9B and C), where the schematic energy levels are based on the reported \( S_0/S_1 \) energy difference of \( \sim 2.5 \text{ eV} \) for \( \text{C}_{60} \) and the \( S_0/T_1 \) energy difference of \( \sim 1.5 \text{ eV} \) for \( \text{C}_{60} \). These schemes are admittedly incomplete, but may serve as a cornerstone for future quantitative studies of radiation chemistry under TEM observation conditions using a high-energy e-beam. Fig. 9A, 1 shows ionization of the \( \pi \)-rich \( \text{C}_{60} \), the standard mechanism of radiation damage (Fig. 1F) (52). We found this path at 103 to 203 K in a dmCNT and consider that it also accounts for the CNT damage at low temperatures (compare Fig. 6A and B). Fig. 9A, 2 illustrates \( \text{C}_{60} \) ionization followed by charge neutralization by prCNT and generation of \( S_0, S_1, \) or \( T_1 \) \( \text{C}_{60} \) (Fig. 1E). We observed this path at 60 kV (36). In prCNT and with 100- to 120-keV electrons (Fig. 9B), the e-beam generates singlet exciton of CNT, and ENT forms \( S_1 \) \( \text{C}_{60} \) (Fig. 1B). However, the 80-keV electron can only form a less-energetic triplet exciton to generate \( T_1 \) \( \text{C}_{60} \) (Fig. 1C). In Fig. 9C, oxCNT generates a triplet exciton and then forms \( T_1 \) \( \text{C}_{60} \) (Fig. 1D). Note that oxCNT has been known to form triplet excitons, probably because of rapid singlet-to-triplet relaxation.

In summary, the kinetics data summarized in Fig. 8 have shown the importance of VT/VV kinetic analysis in the studies of radiation damage. The data also showed that chemical ionization and electron excitation are inseparable, but different, mechanisms of the radiation damage, which have often been classified loosely under the single term “ionization.” The conducting prCNT, with its high-lying filled orbital, not only protects the molecule from radiolysis (8) (Fig. 2C), but can cause selective chemical reactions if suitable orbital interactions between the molecule and the CNT are available. We can account for the mechanism of the five observed reaction types with the standard chemical reaction mechanisms of ionization and excitation without invoking bond scission due to atom displacement, which is known to occur so infrequently that it contributes negligibly to the observed reactions (3) (Fig. 8). The complexity of the kinetics of EII and EIE suggests a risk in making any mechanistic interpretations of chemical events seen using TEM without performing VT/VV kinetic analysis. Enabled by continuous monitoring of chemical reaction events at atomic resolution with variable frame rate (e.g., between millisecond and second), the present research illustrates the potential of “cinematic chemistry,” microscopic imaging of dynamic chemical events, for elucidation of the mechanisms of chemical reactions (24, 40, 53).

Materials and Methods

Materials. Single-walled CNTs (Meijo Arc SO, produced by arc-discharge using Ni and Y catalysts, >99% purity, average diameter 1.4 nm, lot no. 6601316) were purchased from Meijo Nano Carbon Co. Ltd. \( \text{C}_{60} \) powder (nanopure purple ST, >98% purity) was purchased from Frontier Corporation. TEM grids precoated with a lacey microgrid (RO-C15, for VT experiments; pore size 3 to 8 \( \mu \text{m} \) and carbon thickness 70 nm) were purchased from Okenshoji Co., Ltd. Toluene was purchased from Wako Pure Chemical Industries and purified by using a solvent-purification system (GlassContour) (54) equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. Potassium permanganate was purchased from Tokyo Chemical Industry Co., Ltd., and sulfuric acid was purchased from Wako Pure Chemical Industries.

General. The water content of the solvent was determined by using a Karl Fischer moisture titrator (CA-21, Mitsubishi) to be <10 ppm. Bath sonication for the dispersion of CNTs in toluene was carried out with a Honda Electronics WT-200-M instrument. Oxidative removal of the terminal caps of CNTs was carried out in an electric furnace, ASH ARF-30KC. Encapsulation of \( \text{C}_{60} \) into CNTs was carried out in an electric furnace, ASH AMF-20, equipped with a temperature-controller AMF-9P. IR spectra were recorded on a JASCO FT/IR-6100 instrument with attenuated total reflection. X-ray photoelectron spectroscopy analysis was carried out on a JPS-9010MC instrument by using Mg K\( \alpha \) X-rays (1,253.6 eV).

Preparation of Samples for SMART-EM. The \( \text{C}_{60} \)/CNTs prepared above are in solid form and thus difficult to deposit directly on a TEM microgrid. We therefore first dispersed samples in toluene (0.01 mg mL\(^{-1}\)) in vials, which were then placed in a bath sonicator for 1 h. The aim was to soften the samples so that we could secure intimate contact between the CNTs and the carbon surface of the grid. A 10-\( \mu \text{l} \) solution of the dispersion was then deposited on a TEM grid placed...
Ionization of C$_{60}$ to generate an RC at 103 to 203 K in a dmCNT, conducted following a method described in a previous report (19). C$_{60}$ dimerizes by [2 + 2] cycloaddition. Cold-field emission gun (point resolution 0.10 nm) at acceleration voltages of 60, 80, 100, and 120 kV, under 1 kelvin (according to the instrument specifications). The accuracy of the grid temperature was two to three kelvins (according to the instrument specifications). After the stage temperature was raised to the setting value, we waited at least 30 min before commencing observations, in order to stabilize the stage for minimization of thermal drift.

**Data Availability.** All study data are included in the article and/or supporting information.

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