

# Chemical Effects Due to Low-Energy Electron Impact on Thin Films of Cyclohexane and *n*-Hexane at 77°K

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(Received November 1, 1971)

Publication costs assisted by The U. S. Atomic Energy Commission

Films (570–840 Å) of cyclohexane and *n*-hexane at 77°K have been subjected to low-energy electron impact and the products have been analyzed. The yield of bicyclohexyl onsets at  $\sim 8.5$  eV, maximizes at  $\sim 13$  eV, and minimizes at  $\sim 30$  eV. Of the C<sub>12</sub> products from *n*-hexane only *n*-dodecane was resolved in the gas chromatogram. The onset is well below the threshold of optical absorption. Only the *n*-hexane fragment hydrocarbon products ethane, propane, *n*-butane, *n*-pentane, and their congruent olefins (in the order of decreasing yields) were measured in detail. Their yield *vs.* energy profiles were similar with onsets at  $\sim 3.5$  eV, maxima at  $\sim 6.5$  eV, and minima at  $\sim 7.0$  eV. The results for *n*-hexane at low energy are attributed to decompositions from vibrationally excited, low-lying triplet states by direct excitation with spin exchange.

## Introduction

The chemical effects of high-energy radiation tend to be indiscriminate and, with few exceptions, only the ultimate and penultimate products can be characterized and identified. A simple technique has been described to measure the chemical consequences of low-energy electron impact on simple solid molecular systems.<sup>3</sup> Practical considerations require a very low vapor pressure and therefore low temperature. For even modest precision in measurement of the electron energy it is essential to avoid trapping electrons in the target. Consequently, compounds which undergo dissociative electron attachment are not suitable. Since even solid alkanes and alkenes can trap electrons physically, the target should be as thin as possible to minimize this effect.

The present work is concerned with the energy dependence of the yields of bicyclohexyl from cyclohexane, and of *n*-dodecane and C<sub>2</sub>–C<sub>5</sub> alkanes and alkenes from *n*-hexane, under slow electron impact.

## Experimental Section

Samples of cyclohexane (Hinton's Primary Standard Grade 99.98%) and *n*-hexane (Phillip's Research Grade 99.95%) were outgassed and stored on a grease-free vacuum line. From the measured *P*–*V*–*T* of the vapor admitted to the reactor at 77°K the film thickness was  $\sim 570$  Å for cyclohexane and  $\sim 840$  Å for *n*-hexane.

The reactor, a 1-l. Pyrex flask, was inner-surfaced with an evaporated gold film as anode. After rough pumping (mechanical and mercury vapor diffusion pumps) the vacuum handling system, which contained only Pyrex glass, Kovar, and stainless steel, was valved off, baked out, and evacuated to  $2.5 \times 10^{-7}$  Torr by an ion pump. This pressure was also maintained during electron bombardment. A schematic diagram appears in Figure 1. The filament and its mounting have been described.<sup>3</sup>

The filament temperature was adjusted, prior to admitting each sample, to give  $10^{-4}$  A anode current  $I_a$  ( $\sim 2 \times 10^{-7}$  A/cm<sup>2</sup>) at a selected anode voltage  $V_a$ . After admitting a sample the filament was restored to the predetermined temperature gradually over 15 min, then held there  $\sim 3$  min to achieve stability before applying the anode voltage. Tests showed no evidence of pyrolysis. The anode voltage  $V_a$  (*n.b.*, for the bare anode) defines the nominal electron energy for each run and it is used throughout this work unless otherwise explicitly stated. For constant  $V_a$ , *i.e.*, a voltmeter reading,  $I_a$  decreases, mostly during the first few seconds. In the space-charge limited regime this results from a change in the potential difference, presumably due to injected electrons being trapped in the film. It is assumed that increasing  $V_a$  to restore the initial  $I_a$  compensates for this effect, and this adjustment was made as needed throughout each run to maintain constant  $I_a$ .<sup>3</sup> For  $V_a < 10$  V the adjustment was  $< 1$  V.

Independent work with an electron gun operating on its *I*–*V* plateau shows that electron transmission through films of *c*-C<sub>6</sub>H<sub>12</sub> and *n*-C<sub>6</sub>H<sub>14</sub> is not space-charge limited at  $\sim 2 \times 10^{-7}$  A/cm<sup>2</sup>.<sup>4</sup> Consequently, the *I*–*V* characteristics reported previously for the bare anode<sup>3</sup> apply equally for coated anodes, except for a voltage shift.

It is considered preferable to describe the dependence of 100-eV product yields, *G*, in terms of onsets, rather than peaks, in the *G*(product) *vs.* *V* spectra. As a

(1) This work is based on a dissertation submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Notre Dame.

(2) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-813.

(3) L. M. Hunter, T. Matsushige, and W. H. Hamill, *J. Phys. Chem.*, **74**, 1883 (1970).

(4) K. Hiraoka, work in progress at this laboratory.

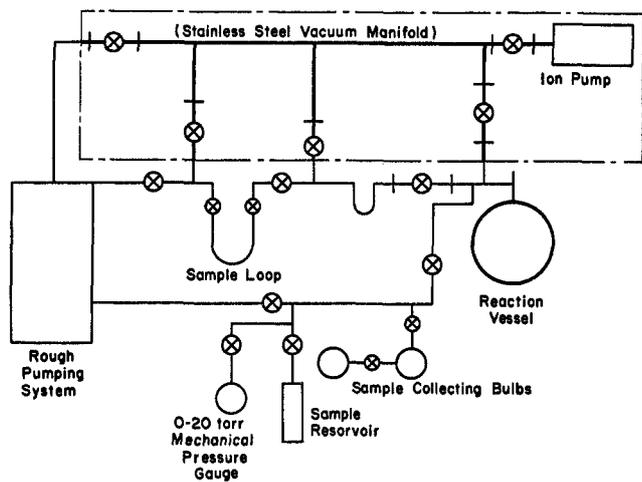


Figure 1. A schematic diagram of the apparatus used for low-energy irradiation of cyclohexane and *n*-hexane by electron impact.

consequence, one-half the  $IR$  drop along the filament ( $IR \cong 1.5$  V) and an additional Boltzmann spread will introduce a rather large low-energy shift in onsets relative to voltmeter readings. The effect of contact potentials cannot be assessed for the equipment used, but it is known that relative to a given cathode, contact potentials for several alkanes and alkenes are the same.<sup>4</sup>

From five to ten runs were performed at each electron energy, the average deviation of yields amounting to 15–20%. Sample collection and analysis have been described.<sup>3</sup>

## Results

The only product from cyclohexane in the region of higher boiling compounds in the gas chromatogram (with a silicone gum rubber SE-30 column) was bicyclohexyl. Small yields of cyclohexyl-hexane and cyclohexyl-cyclohexene are produced by  $\gamma$  irradiation. (The yield of cyclohexene could not be measured on the same column and circumstances did not allow an additional  $10^2$  experiments.) The yield of bicyclohexyl was linear with dose over a considerable range at low electron energy, *e.g.*, to  $\sim 10^{-21}$  eV/g. At higher electron energy the yield-dose curve fell off more rapidly. All yields are reported for the linear region.

The electron-energy profile of the yield of bicyclohexyl appears in Figure 2. By rough extrapolation from the initial steep rise the onset is  $\sim 8.5$  eV. There are small yields of bicyclohexyl at low energy, amounting to 2, 2, 5, 28, and 76 in units of molecules/ $10^5$  eV at 4, 5, 6, 7, and 8 eV. The maximum is  $G(\text{bicyclohexyl}) = 0.43$  at 13 eV, compared to  $G = 1.55$  for  $\gamma$  irradiation at 77°K.<sup>5,6</sup>

Of the  $C_{12}$  products produced by electron impact on thin films of *n*-hexane only *n*-dodecane could be fully resolved by gas chromatography. Although this compound contributes  $<10\%$  to the combined  $C_{12}$  yield,

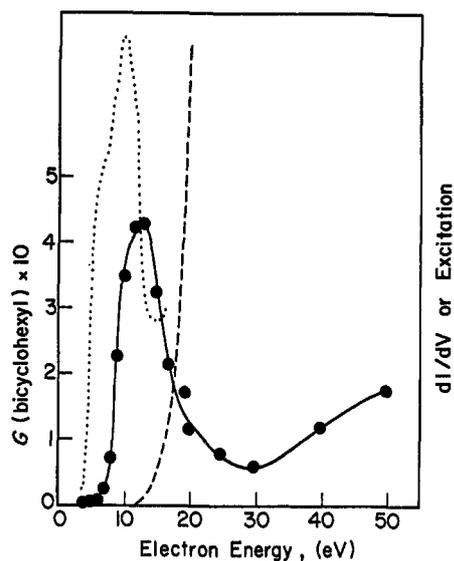


Figure 2. The electron energy profile of the 100-eV yield of bicyclohexyl from cyclohexane (●); the excitation curve for 490-nm emission (---), and the spectrum  $dI_a/dV_a$  vs.  $V_a$  (...) for cyclohexane.

this limited information is adequate for the present purpose since there is a nearly uniform  $G$ - $V$  dependence for the entire group. The results, limited to the very low energy range, appear in Figure 3. The onset occurs at  $\sim 2$  eV (nominal). The yield for  $\gamma$  irradiation at 77°K is included for comparison.

Of the alkane and alkene fragment products from *n*-hexane, only propane and propene could not be resolved while methane was not retained during recovery of the sample prior to analysis. The results for ethane and ethylene were badly scattered at 3 eV and the yields of all fragment products are small and inaccurate at 2 V, but circumstances did not permit further work. The results in Figure 4 still provide evidence for a maximum in the yield of ethane at  $\sim 3$  eV in addition to that at 6 eV. The yields of ethylene (not shown) were 10–20% of the yields of ethane. The energy profiles for the combined  $C_3$ 's in Figure 5 and for butane and butene in Figure 6 follow the same pattern as ethane. The profiles for pentane and pentene in Figure 5 differ only at  $\geq 10$  eV.

A brief examination of 1,3-cyclohexadiene under electron impact at 3.0, 4.0, and 4.5 eV showed that benzene was a product at each energy and the largest yield,  $G(C_6H_6) = 0.6$ , occurred at 4.0 eV.

## Discussion

Characteristic energy losses by electrons in solids are quantized, distinctive of the substance and independent of the incident electron energy and of the target thickness. For thin films these losses can be measured

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(6) A. Charlesby, *Intern. J. Radiat. Phys. Chem.*, **1**, 45 (1961).

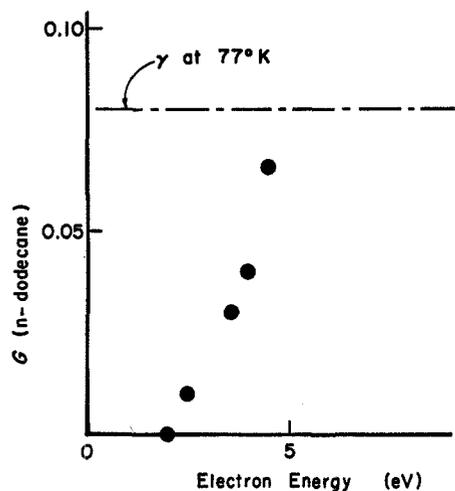


Figure 3. The electron energy profile of the 100-eV yield of *n*-dodecane from *n*-hexane. The yield of *n*-dodecane from  $\gamma$  irradiation at 77°K is included for comparison.

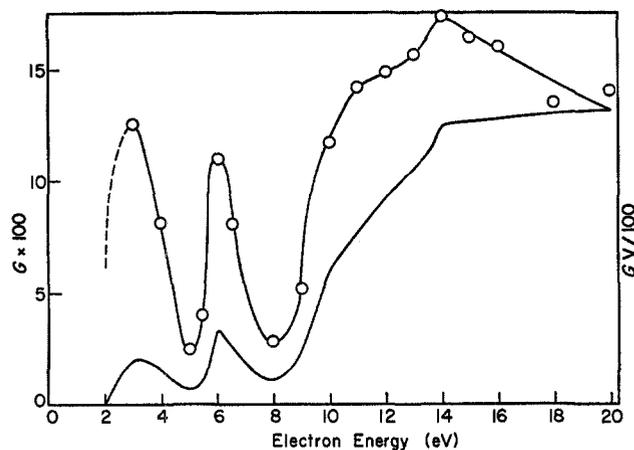


Figure 4. The electron energy profile of the 100-eV yield of ethane from *n*-hexane (O) and the corresponding dependence for  $GV_a/100$  (—).

directly by energy analysis of backscattered electrons,<sup>7</sup> or indirectly from structure in curves of  $dI_a/dV_a$  vs.  $V_a$ .<sup>4,8</sup> The reliability of the method has been tested on several aromatic compounds for which optical and photoelectron spectra have been measured. For a total of 37 energy levels the methods agree within  $\sim 0.1$  V, on the average.<sup>4</sup> Data for such electron impact measurements have been included in Figure 2 where it can be seen that they correlate in part with visual estimates of  $dG/dV_a$  vs.  $V_a$ . It is not possible to allow for the contact potential difference between a tungsten filament used in this work and a rhenium filament coated with lanthanum hexaboride.<sup>4,7</sup> It is clear, nevertheless, that there are characteristic electron energy losses to cyclohexane well below the onset of optical absorption. In cyclohexane this energy is not efficiently utilized, unlike earlier results for hexene-1<sup>3</sup> and present results for *n*-hexane.

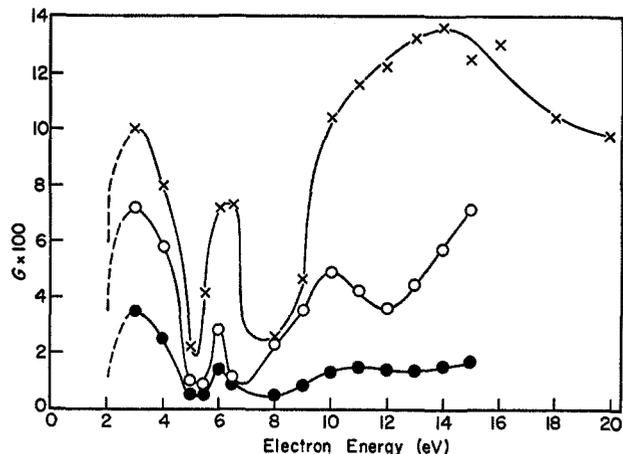


Figure 5. The electron energy profile of the 100-eV yields of combined propane and propene (x), of *n*-pentane (O), and O, *n*-pentene (●).

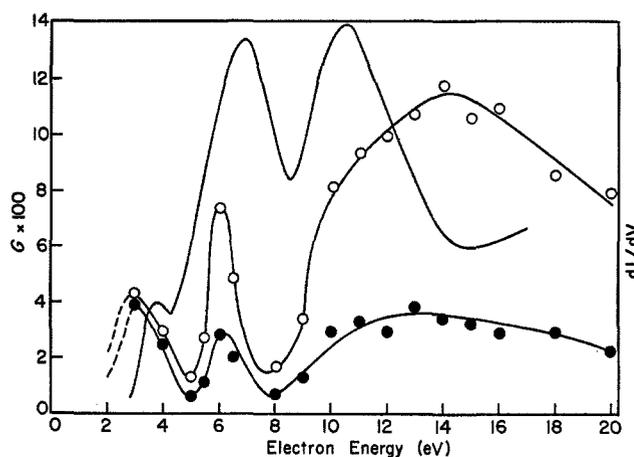


Figure 6. The electron energy profile of the 100-eV yields of *n*-butane (O) and *n*-butene-1 (●) from *n*-hexane. The upper curve (from ref 4) is  $dI_a/dV_a$  vs.  $V_a$  for *n*-hexane.

The yields of bicyclohexyl from cyclohexane are very small below  $\sim 8$  eV. Consequently, low-lying triplet states of cyclohexane contribute negligibly to chemical yield, although they do contribute appreciably to electron energy losses.<sup>4</sup>

The yield of bicyclohexyl drops rather sharply at 13 eV and the small yields of bicyclohexyl above  $\sim 20$  eV may be a consequence of increasing yields of cyclohexene, but this is not supported by other work. Batten<sup>9</sup> has measured the formation of hydrogen from cyclohexane at 77°K under electron impact. The onset at  $\sim 7.5$  eV was attributed to elimination of H and H<sub>2</sub> from an excited neutral, and this may correlate with the onset for bicyclohexyl formation. It appears to be unlikely that a higher onset in formation of hy-

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(8) L. M. Hunter, D. Lewis, and W. H. Hamill, *ibid.*, **52**, 1733 (1970).

(9) C. F. Batten, Ph.D. Thesis, University of Notre Dame, 1971.

drogen at  $\sim 18$  eV can be attributed to a process producing molecular hydrogen which would compete with formation of bicyclohexyl. The low yields may be an artifact of thin films caused by the migration of excited states to the anode at which they would be quenched, but this is not indicated by related studies of luminescence.<sup>9,10</sup>

Under slow electron impact, thin films of cyclohexane at 77°K emit at 210, 360, and 490 nm,<sup>10</sup> the relative intensities being  $\sim 1$ , 1.5, and  $>10^2$ . The onset of excitation for the 490-nm band was  $\sim 12.5$  eV. Although the other bands were too weak for measurement near onset, it was observed that the intensity of the 210-nm band decreased at  $>15$  eV and was not detectable at 25 eV. In a rough way this follows the behavior of  $G(\text{C}_{12}\text{H}_{22})$  vs.  $V$  and suggests that 210-nm fluorescence and cyclohexyl radicals arise from a common state, or set of states. The quantum yield for 201-nm fluorescence of cyclohexane at 298°K is 0.0035,<sup>11</sup> and it should not be less at 77°K. If the cross sections for excitation of the thin film states emitting at 210 nm and 490 nm are comparable, then the probability of emission at 490 nm from  $>3$ -eV excited states produced by electron impact at  $>12.5$  eV may approach unity. That is, luminescence may compete effectively with chemical decomposition. The excitation curve for 490-nm luminescence,<sup>9,10</sup> included in Figure 2, is expressed in terms of uncorrected electron energies. The excitation curve suggests that luminescence arises from an excited state of the molecular ion. This state does not contribute appreciably to the yield of bicyclohexyl since it cannot be excited below  $\sim 12.5$  eV. The final state of the electronic transition is expected to be the ground state of the molecular ion, and this cannot be a major precursor of bicyclohexyl since luminescence competes with decomposition. Recalling that 210-nm luminescence decreased as 490-nm intensity increased, it may be proposed that the 210-nm fluorescing state does not have ground-state molecular ion as a major precursor, and that it is the principal precursor of bicyclohexyl.

The cross section for excitation by electron impact typically reaches a maximum within a few volts of onset, then declines gradually. The dependence of  $G(\text{bicyclohexyl})$  vs.  $V_a$  is consistent with the assumption that excited singlet states are responsible since it resembles the excitation function for a state, or narrow group of states. The onset of ionization does not compete strongly because the cross section for ground state ion is small for the first few electron volts. Finally, several excited states of the ion are available with cross sections still increasing at  $\sim 14$  eV and  $G(\text{singlets})$  falls rapidly by competition. One further assumption is that ion-electron combination produces fewer singlets than direct impact. Since triplets do not contribute to  $G(\text{C}_{12}\text{H}_{22})$ , and charge combination yields mostly triplets, this is plausible.

The results for *n*-hexane provide more detailed information than the preceding. The yields of all products provide evidence for energy deposition by electrons at  $<4$  eV, *i.e.*, well below the threshold for optical excitation. There is no known mechanism whereby slow electrons can rupture C-C and C-H bonds by energy transfer to a high vibrational level of the neutral ground-state alkane. Electronic excitation must be invoked and low-lying triplet states are postulated, for which there is other evidence.<sup>4,7,8,12</sup>

If it is assumed that the precursor of *n*-dodecane at low energy is *n*-dodecyl, then the bond dissociation energy  $D(\textit{n-C}_{12}\text{H}_{25}\text{-H}) \cong 4.3$  eV requires an energy scale shift of  $\sim 2.3$  eV in Figure 3. If the onsets of the  $\sim 6$ -eV peaks in Figures 4-6 are attributed to the lowest excited singlet states, then the average of the corresponding onsets at 5.2 eV must also be shifted by  $\sim 2.3$  eV to match the onset of optical absorption of *n*-hexane at 7.4 eV.<sup>13</sup> The shift arises in part from the work function of the emitter, the bulk electron affinity of the target, and the trapped charges therein. It depends also on the arbitrary choice of a point on the  $I$ - $V$  characteristic for the bare anode, on the  $IR$  drop in the filament, on the high-energy tail of the Boltzmann, and on the necessity of measuring onsets. Clearly, internal standards must be adopted.

Characteristic electron energy losses for *n*-hexane would provide appropriate internal standards but they could not be measured under the experimental arrangements used in this work. They have been measured<sup>4,7,8</sup> and, together with other work,<sup>12</sup> locate the lowest alkane triplet states well below the bond dissociation energies. The spectrum of  $dI/dV$  vs.  $V$  in Figure 6 shows these losses for slow electrons injected thermionically into a thin film of *n*-hexane at 77°K.<sup>4,8</sup> Consequently, in the present work the lower excited vibronic levels are not expected to give measurable products. Rather, excitation must reach a point on the first triplet potential energy surface at least as high as the asymptote along which the specified radical pair can separate in their ground states to form the observed products. Under favorable conditions the appearance potentials for these products will be equal to the corresponding bond dissociation energies along the ground state singlet surface. The two surfaces converge rapidly as the radical-radical separation increases since a singlet pair of doublets will have the same energy as a triplet pair of doublets.

It is assumed that decomposition of *n*-hexane from the lowest vibronic level of the first excited singlet state is possible and that the appearance potentials

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(11) F. Hirayama and S. Lipsky, *ibid.*, **51**, 3616 (1969).

(12) D. Lewis and W. H. Hamill, *ibid.*, **52**, 6348 (1970).

(13) J. W. Raymond and W. T. Simpson, *ibid.*, **47**, 430 (1967).

at  $\sim 5.0$  eV (nominal) in Figures 4–6 are characteristic of the state and not of the bond. The higher onsets at  $\lesssim 8$  eV (nominal) must then be shifted by 2.3 eV to  $\lesssim 10.3$  eV, which suggests that ionization is responsible, and quite possibly an excited state of the ion. If polarization lowers the energy required for ionization in the film, the excess energy at onset in  $C_6H_{14}^{+*}$  is  $\sim 1.3$  eV. This approximates the energy required for fragmentation.

The fluctuations in electron energy utilization for production of some products (Figures 4–6) cannot be reliably accounted for because there may be balancing changes in the yields of products not measured. Since the combined yield of all hydrocarbon products from  $\gamma$  irradiation at 77°K corresponds to 4.5 molecules of *n*-hexane decomposed per 100 eV absorbed, and only 9% appears in  $C_2$ – $C_5$  products,<sup>14</sup> such competition is quite possible. On the other hand, characteristic energy losses are markedly energy dependent and this requires some corresponding changes in  $G$  vs.  $V$ .

Luminescence from *n*-hexane at 77°K with  $\lambda_{max}$  490 nm is excited by electron impact with an onset at  $\sim 12.5$  eV.<sup>10</sup> The emitting state may be the highest of the first group of excited states of alkane ions.<sup>15</sup> Since they can be observed by mass spectrometry,<sup>16</sup> but at rather low abundance, luminescence may compete with unimolecular decomposition. The intensity of 490-nm luminescence is  $\sim 200$  times that at 210 nm. The quantum yield for 207-nm fluorescence under rather different conditions (1470-Å excitation and 298°K) is  $2 \times 10^{-4}$ .<sup>11</sup> This suggests that the efficiency of 490-nm emission may be very small and so not compete with decomposition.

The yields of fragment products from *n*-hexane also decrease at  $\gtrsim 14$  eV, but not nearly as markedly as  $G(\text{bicyclohexyl})$  in the same interval. In fact, if the electron yields are expressed as molecules of product

per electron impact, *i.e.*,  $GV_a/100$ , then the yields are nearly constant in the interval 14–25 eV. For each of the products in Figures 4–6, the electron yields at 25 eV (not shown) are very nearly the same as those at 15–20 eV.

Taking ethane as a representative product, and considering the electron yield profile, it can be inferred that ground-state ions are not efficient precursors of product. That is, they neither decompose efficiently as ions nor upon subsequent neutralization.

The formation of  $C_2$ – $C_5$  products as well as *n*-dodecane below 5 eV is considered to be evidence for low-lying triplet states of *n*-hexane. This interpretation is supported by evidence from mass spectrometry for an excited state of *n*-hexane at 2.8 eV.<sup>17</sup> It is also consistent with 4.4-sec recombination luminescence from 3-methylpentane<sup>18</sup> and with slow electron energy losses for *n*-hexane, cyclohexane, and 3-methylpentane.<sup>7,8</sup> If the lowest potential energy surface for triplet *n*-hexane were repulsive for all molecular configurations the minimum vertical excitation energy would be rather greater than the minimum bond dissociation energy, contrary to observation. Neither would such an assumption be able to account for a slow recombination luminescence. Consequently, it is assumed that vertical excitation to a low-lying triplet potential energy surface and Franck–Condon effects may produce either a stable slow emitter or a radical pair, depending upon the vibrational excitation.

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(16) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 546 (1964).

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