and from d[H]/d*t*

$$R_{(n+i)} = 2(k_3 + k_4)[(\mathrm{HgC_3H_8})^*] + 2(k_8 + k_9)[(\mathrm{HgC_3H_8})^0]$$

or

$$R_{(n+i)} = 2(k_{12} + k_{13})[\mathrm{H}][\mathrm{C_3H_8}]$$

Division of $R_{(n)}$ by $R_{(n+i)}$ including the contribution from the nonuniform absorption of light[25] gives

$$2R_{(n)}/R_{(n+i)} = Q_4 + k_{13}/(k_{12} + k_{13}) - \delta Q_3 \quad (28)$$

where

$$\delta = \frac{2\{1 - \exp(-\epsilon[\mathrm{Hg}]L/2)\}}{\{\epsilon[\mathrm{Hg}](1 - \exp(-\epsilon[\mathrm{Hg}]L))\}}$$

L is the path length (4 cm) and ϵ is the extinction coefficient of mercury.

$$Q_3 = \{k_{14}[n\text{-Pr}] - k_{-14}[i\text{-Pr}]\}[\mathrm{C_3H_8}]/R_{(n+i)} = \frac{R_{\mathrm{DMB}}{}^{1/2}}{R_{(n+i)}}\left(\frac{R_{\mathrm{MP}}}{R_{\mathrm{DMB}}} - 2K_{14}{}^{-1}\right)\frac{k_{14}}{k_{19}{}^{1/2}}[\mathrm{C_3H_8}]$$

and

$$Q_4 = \frac{k_4[(\mathrm{HgC_3H_8})^*] + k_9[(\mathrm{HgC_3H_8})^0]}{(k_3 + k_4)[(\mathrm{HgC_3H_8})^*] + (k_8 + k_9)[(\mathrm{HgC_3H_8})^0]}$$

From eq 29 and 31, Q_4 is given by

$$Q_4 = \frac{\dfrac{k_4k_2[\mathrm{Hg}^*]}{(k_3 + k_4 + k_5 + k_6)} + \dfrac{k_9k_7[\mathrm{Hg}^0]}{(k_8 + k_9 + k_{10})}}{\dfrac{(k_3 + k_4)k_2[\mathrm{Hg}^*]}{(k_3 + k_4 + k_5 + k_6)} + \dfrac{(k_8 + k_9)k_7[\mathrm{Hg}^0]}{(k_8 + k_9 + k_{10})}}$$

Dividing the numerator and denominator by $k_7[\mathrm{Hg}^0]$ and substitution of F, Φ^*, and Φ^0 yield

$$Q_4 = (F\Phi^* + \Phi^0)^{-1}\left\{\frac{k_4F}{(k_3 + k_4 + k_5 + k_6)} + \frac{k_9}{(k_8 + k_9 + k_{10})}\right\} = \frac{k_4}{k_3 + k_4}\beta + \frac{k_9}{k_8 + k_9}(1 - \beta)$$

where

$$\beta = \Phi^*F/(F\Phi^* + \Phi^0)$$

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(25) Reference 6, p 640.

The Mechanism of Energy Transfer in the Triplet Mercury Photosensitization of Paraffins

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Abstract: A unified mechanistic model accommodating all known experimental observations is proposed for the quenching of the $^3P_1$ and $^3P_0$ states of mercury atoms by the paraffins. The process is viewed as a simple hydrogen abstraction reaction of the divalent, paramagnetic mercury atom in analogy with the well-characterized abstraction reactions of other triplet (but ground state) reagents such as O (^3P), carbenes, nitrenes, etc. The principal differences between ground- and excited-state systems can be summarized in the following points. (i) The excited state transition complex is more stable owing to the higher polarizability of the excited atom as compared to that of ground-state species, has a longer lifetime, and is capable of undergoing radiative transitions, making it amenable to experimental observations through spectroscopic studies. (ii) The presence of a larger number of reaction channels in the excited state renders the excited state chemistry more complex and causes a pronounced departure from simple second-order kinetics on the microscopic scale. The semiempirical bond-energy–bond-order method for the estimation of the energy of activation of ground-state systems can also be applied with appropriate minor modifications to the Hg ($^3P_1$) paraffin systems. The computed energies of activation correctly predict the trend in the experimental rate data.

Early studies on the triplet mercury photosensitized reactions of paraffins date back nearly to the time of discovery of the phenomenon of electronic energy transfer.[1,2] In the intervening years an immense amount of work has been expended on the experimental study of the field. The problems actively explored were centered on the nature of the primary steps involved, together with their quantum efficiencies and absolute rate parameters, the role of the lower lying metastable $^3P_0$ (Hg^0) state of mercury in the reaction sequences, and in a more general context, on the elucidation of the details of the reaction hypersurfaces. To these were later added the spectroscopic problems related to the phenomena of pressure broadening and band fluorescence from the transient complexes formed between the mercury atom and paraffin molecule.

The theoretical framework for the rationalization of the mechanistic details evolved slowly. This can be attributed to several factors. The reactions of electronically excited atoms, as photochemical systems in general, proceed on excited surfaces involving radiative and nonradiative internal transitions. The transition probabilities and the potential surfaces themselves, apart from a few exceptions, are poorly characterized. Therefore conventional rate theories are not readily applicable and because of the high atomic number of

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(1) A. G. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Macmillan, New York, N. Y., 1934.

(2) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, Chapter II.

mercury the systems do not lend themselves to rigorous quantum mechanical treatments either. Moreover, experimental data reported until quite recently have often been fragmentary, unreliable and self-conflicting. Some kinetic parameters have been measured redundantly while others were grossly neglected.

The salient kinetic features established for the triplet mercury + paraffin systems may be summarized in the following points. (i) Interaction of Hg ($^3P_1$) (Hg*) atoms with paraffins leads to the decomposition of the paraffin. The sole primary step consists of C–H bond cleavage with the complete absence of C–C rupture (cyclopropanes excepted). The quantum efficiency of decomposition at room temperature, apart from the cases of methane and ethane, is nearly unity. (ii) The quenching rate constants, especially for the smaller paraffins, are all lower than the gas kinetic collision frequency and the molecular rate constants are the sums of the specific increments which can be assigned to each C–H bond in the molecule. These vary in the order k(tertiary CH) > k(secondary CH) > k(primary CH). The primary yields of the various possible alkyl radicals are in the ratio of the quenching efficiencies of the respective CH bonds in the molecule, which in turn correlate with the strength of the bond. (iii) Parallel to decomposition, spin–orbit relaxation of the Hg* atom to the ($^3P_0$) state also occurs. The efficiency of this step varies with temperature and the nature of the paraffin. With propane, the activation energies for the formation of Hg^0 atoms, *n*-propyl, and isopropyl radicals, decrease in the order of presentation. (iv) Deuteration of the quenching site causes a large direct kinetic isotope effect in the quenching process and enhances Hg^0 atom production. (v) Every paraffin displays a more or less intense band fluorescence in the neighborhood of the 2537-Å mercury resonance line, the carrier of which is the excited complex formed between the Hg* atom and a paraffin molecule. There is an inverse relationship between the intensity of fluorescence and the decomposition quantum yield. (vi) The Hg^0 atom sensitized decomposition of paraffins also leads to exclusive C–H bond cleavage. The quantum yield at room temperature is less than unity and the deficiency is not due to bond fluorescence, but rather to an intersystem crossing of the triplet excited (Hg·RH)* complex to the ground electronic state with the consequent dispersion of the electronic energy into the vibrational, rotational, and translational degrees of freedom. With increasing temperature the quantum yield of decomposition increases to unity. (vii) The Hg 6($^1P_1$) atom sensitized reactions of paraffins also lead to decomposition *via* C–H bond cleavage but these atoms are less discriminative with respect to C–H bond energy than triplet atoms are. Parallel to decomposition, relaxation to the triplet manifold probably also occurs.

The first attempt to rationalize quenching data was made by Magee and Ri[3,4] who emphasized the importance of the intersection of the initial potential energy surface with the polar surface that correlates with the final state.

Laidler[5] first suggested that the quenching reactions of electronically excited atoms be treated in terms of excited potential energy surfaces. Accordingly, the system was considered as ending up on a surface leading to HgH + R after intersecting a number of relevant excited surfaces. Naturally, only qualitative conclusions were possible because the relevant information needed to construct these excited surfaces was not available.

Gunning and Strausz[6] pointed out the electrophilic nature of the Hg* atom and suggested a correlation between nucleophilicity and quenching efficiency of the energy acceptor. The large H/D kinetic isotope effect observed in the quenching by paraffins was found to be accountable in terms of absolute reaction rate theory, wherein the magnitude of this effect is determined by the difference in zero-point energy between the C–H and C–D bonds.

The role of the long-lived transient complexes formed between the excited Hg atom and the energy acceptor was emphasized by Penzes, Strausz, and Gunning.[7]

Yang[8] attributed the differences in the quenching rates of Hg* atoms with hydrogen and paraffins to the stability and structure of the collision complex. According to this model, the decomposition rate constant of the complex to products was given by the Kassel equation of unimolecular reactions.

$$k_q \simeq k_d = A\left(\frac{E_T - E_0}{E_T}\right)^{s-1}$$

where A is the frequency factor, E_0 is the critical energy of decomposition, taken to be equal to the bond dissociation energy from the zeroth vibrational level, E_T is the excitation energy of mercury, and s is the number of the effective classical oscillators. This equation yields a large value of k_d for hydrogen but a small value for paraffins, relative to dissociation of the complex back to reactants, in superficial agreement with experiment. Furthermore, from symmetry correlations between reactants, products, and the intermediate reaction complex, Yang concluded that the deactivation of metastable mercury atoms to the ground state was allowed by paraffins but forbidden for the reaction with hydrogen, whereas the quenching of Hg* by both species was symmetry allowed. The enhanced formation of Hg^0 atoms on deuteration of the paraffins was explained in terms of phase-space theory whereby the spin–orbit energy is transferred into rotational degrees of freedom. Recent measurements on the quenching of Hg^0 and Hg* atoms by hydrogen[9,10] and paraffins[11] have created serious doubts about these explanations, however.

Vikis and Moser[12] investigated the quenching of excited mercury atoms ($^1P_1$, $^3P_1$, $^3P_0$) by alkanes using the RRKM theory of unimolecular reactions. The model was based on the formation of a relatively long-lived excited mercury–alkane complex on a potential energy surface leading to decomposition of the complex by C–HHg bond rupture. In order to apply RRKM theory in a fashion capable of yielding quantitative pre-

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(3) J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

(4) J. L. Magee and T. Ri, *ibid.*, **9**, 638, (1941).

(5) K. J. Laidler, *ibid.*, 10, 34, 43 (1942).

(6) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 209 (1963).

(7) S. Penzes, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **45**, 2322 (1966).

(8) K. Yang, *J. Amer. Chem. Soc.*, **87**, 5294 (1965); **89**, 5344 (1967).

(9) T. L. Pollock, E. Jakubowski, H. E. Gunning, and O. P. Strausz, *Can. J. Chem.*, **47**, 3474 (1969).

(10) A. B. Callear and J. C. McGurk, *Chem. Phys. Lett.*, **7**, 491 (1970); **6**, 417 (1970).

(11) J. M. Campbell, H. E. Gunning, and O. P. Strausz, *Can. J. Chem.*, **47**, 3763 (1969); *J. Amer. Chem. Soc.*, **95**, 740 (1973).

(12) A. C. Vikis and H. C. Moser, *J. Chem. Phys.*, **53**, 2333 (1970).

dictions, the authors were forced to make so many arbitrary assumptions as to leave little credibility in the results.

In the present article it is shown that the triplet mercury atom sensitized decomposition of paraffins can be considered as a simple hydrogen atom transfer reaction and consequently it is possible to calculate potential energies of activation for these reactions by a slightly modified bond-energy–bond-order (BEBO) method.[13]

Modified Bond-Energy–Bond-Order Calculations

In the BEBO method, the potential energy of activation for H atom abstraction by a radical as a function of bond order n is given by

$$V = E_{1s}(1 - n^p) - E_{2s}(1 - n)^q + V_{tr}$$

where E_{1s} and E_{2s} are the single bond energies of the bond being broken and formed, V_{tr} is the triplet repulsion term, and p and q are the bond energy indices defined by the expression

$$p \text{ or } q = \frac{0.26 \ln (D_e/\epsilon_x)}{r_x - r_e}$$

in which ϵ_x and r_x are the potential depth and the equilibrium internuclear distance of the analogous diatomic noble gas cluster, and D_e and r_e are the bond dissociation energy and equilibrium internuclear distance of the bond in question. Mayer and Schieler[14] successfully extended the original BEBO method by the introduction of slight modifications, to the reactions of O atoms in the ^3P and ^1D states with hydrocarbons. In order to calculate relative potential energies of activation for the mercury photosensitized decomposition of paraffins the following model is assumed.

$$\mathrm{R{-}H + Hg^* \longrightarrow R\underset{r_1}{\cdots}H\underset{r_2}{\cdots}Hg \longrightarrow R + H{-}Hg}$$

Here the paraffin is approximated as a diatom, R–H, and the excited mercury is considered as a radical. The Hg–H molecule is assumed to be the final product with a bond energy equal to the sum of the electronic energy of the excited mercury atom plus the heat of formation of Hg–H including zero-point energy. Lennard-Jones force constants of the Hg–He pair are used to calculate the bond energy index of the Hg–H molecule, and since the magnitude of the repulsive triplet term V_{tr} could not be estimated, it was neglected. The results are compiled in Table I. Since the model assumed is somewhat oversimplified and absolute numbers with which to compare computed values are nonexistent, only the relative values are significant. The success of this approach lies in its ability to predict the experimentally observed trends in the Hg^0 and Hg^* sensitization of propane and other representative paraffin systems.

Discussion

It is now possible to formulate a unified mechanistic model for the quenching of $Hg(^3P)$ atoms by the paraffins. The basic mechanism is comprised of the following elementary steps.

$$\mathrm{Hg^* + HR \longrightarrow (Hg{\cdot}HR)^{*\dagger}} \tag{1}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} \longrightarrow Hg^* + HR} \tag{2}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} \longrightarrow HgH + R} \tag{3}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} \longrightarrow HgH + R'\ (or\ R'',\ R''',\ etc.)} \tag{4}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} \longrightarrow Hg^0 + HR} \tag{5}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} \longrightarrow Hg{\cdot}HR} + h\nu \tag{6}$$

$$\mathrm{(Hg{\cdot}HR)^{*\dagger} + M \longrightarrow (Hg{\cdot}HR)^* + M} \tag{7}$$

$$\mathrm{(Hg{\cdot}HR)^* \longrightarrow Hg{\cdot}HR} + h\nu' \tag{8}$$

$$\mathrm{Hg^0 + HR \longrightarrow (Hg{\cdot}HR)^{0\dagger}} \tag{9}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} \longrightarrow Hg^0 + HR} \tag{10}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} \longrightarrow HgH + R} \tag{11}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} \longrightarrow HgH + R'\ (or\ R'',\ R''',\ etc.)} \tag{12}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} \longrightarrow Hg{\cdot}HR} + h\nu''\ (?) \tag{13}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} \longrightarrow Hg + HR} \tag{14}$$

$$\mathrm{(Hg{\cdot}HR)^{0\dagger} + M \longrightarrow Hg + HR + M(?)} \tag{15}$$

Table I. Calculated Potential Energies of Activation for the Reactions of Excited Mercury Atoms with Different Reagents Using Attractive Term Only[a,b]

Reagent	$D_e(R{-}X)$[c]	$^3P_0$	$^3P_1$	$^1P_1$
$CH_3{-}H$	108.2	9.7	8.5	3.1
$C_2H_5{-}H$	102.1	7.6	6.6	2.4
$(CH_3)_2CH{-}H$	98.7	6.5	5.7	2.1
$(CH_3)_3C{-}H$	95.1	5.5	4.8	1.7
$(CH_3)_3CCH_2{-}H$	103.2	7.9	6.9	2.5
$CClH_2{-}H$	104.8	8.5	7.4	2.7
$CH_3{-}Cl$	84.9	0	0	0
$CFH_2{-}H$	105.3	8.6	7.5	2.8
$CH_3{-}F$	109.6	5.6	5.1	2.6
$CF_3{-}F$	129.3[d]	10.4	9.5	4.9

[a] The Hg*–X bond energy is taken to be equal to the excitation energy of the excited mercury atom plus D_e(Hg–X). The values used for X = H (10.6), F (42.2), and Cl (23.4) are in kcal/mol. [b] The bond energy index calculated for the Hg ($^3P_1$)–X bond was used throughout. Values used are C–H = 1.087, ref 13; C–Cl = 0.995, C. M. Previtali and J. C. Scaiano, *J. Chem. Soc. B*, 2317 (1971); C–F = 1.028; Hg*–H = 1.279; Hg*–Cl = 1.068; Hg*–F = 1.357. For the mercury–helium diatomic cluster the values of ϵ_x = 0.19 kcal/mol and r_x = 3.06 Å were used: J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954, pp 1110–1112. [c] Bond energies (kcal/mol) include zero-point energies: J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [d] J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, **63**, 2656 (1967).

The reactants, Hg^* or Hg^0 and RH combine along an attractive potential surface with interaction energies which are proportional to the overall polarizability of the reactants. A schematic illustration of the processes in terms of simplified potential energy curves is given in Figure 1. It is assumed in the reaction scheme and in the potential curve illustration that only one type of complex is formed between excited mercury and the paraffin. In fact, mercury may be bound to one specific hydrogen atom in the complex; hence in the case of paraffins containing distinguishably different hydrogens, more than one type of complex may be involved. These would represent an array af analogous potential surfaces each of which would be predissociative with intersections to the respective repulsive surfaces leading to R, R′, or R″, etc., + HgH formation. In the case of the Hg^* atoms additional splitting of the attractive surfaces may occur since the **J** vector, under the influence of an external perturbation, may take

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(13) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966, p 339.

(14) S. W. Mayer and L. Schieler, *J. Phys. Chem.*, 72, 2628 (1968).

three different orientations. Approximating the paraffin with the diatom RH, and assuming that the complex belongs to the C_s point group symmetry, three surfaces, two A′ and an A″ result. Finally, the situation may be further complicated by the doubling of the R + HgH surfaces if spin–orbit splitting of the alkyl radicals is considered.

Redissociation of the complex, step 2, occurs to some extent even with the more reactive paraffins since the overall quenching rate constant is lower than the gas kinetic value.

Predissociation *via* steps 3 and 4 leads to chemical decomposition of the hydrocarbon. The formation of HgH rather than Hg + H is not a crucial point and recently the presence of HgH has been detected in a number of paraffin systems.[15] The height of the crossing points of the dissociative states, which governs the quenching efficiency, is determined primarily by the interaction energy of the complex, ϵ^*, and the C–H bond strength. The crossing point lies lowest for the weakest C–H bond and successively higher for the stronger ones. The difference in the heights, ΔE^*, governs the relative quenching efficiencies of the various types of C–H bonds in the molecule and the relative yields of the alkyl radicals produced in the primary step.

Concurrent with predissociation is internal conversion to the lower lying $(Hg\cdot HR)^0$ surface, followed by dissociation to Hg^0 + RH, step 5, radiative transition to the ground state, step 6, and collisional stabilization, step 7.

This, however, cannot be the mechanism by which deuteration enhances the yield of Hg^0 atom formation. The latter phenomenon suggests the existence of an additional low energy pass, indicated by the dotted line in Figure 1, connecting the $(Hg\cdot HR)^*$ and $(Hg\cdot HR)^0$ surfaces. This could be the A″ component of the states with which the Hg* + HR correlates and thus the transition would be symmetry allowed. Deuteration then, owing to the lower zero-point energy, would have the effect of favoring the lower energy paths, Hg^0 formation, over predissociation. An interesting corollary of this proposition is the possibility of predissociation of the $(Hg\cdot HR)^0(A'')$ complex formed from Hg* atom, that is, Hg* sensitization following the path of Hg^0 sensitization. Quenching cross section and quantum yield data are in agreement with this model. Thus, the physical quenching cross sections of C_2H_6 (~0.2 Å^2) and C_2D_6 (~0.2 Å^2)[16] are approximately equal because the major processes in quenching Hg* atoms are band fluorescence and Hg^0 atom formation. On the other hand the quenching of Hg* atoms by propane is sensitive to deuterium substitution ($\sigma^2(C_3H_8) \sim 3.1$ and $\sigma^2(C_3D_8) \sim 0.88$ Å^2)[16] since in this case the major mode of quenching is *via* predissociation.

The radiative transition of the $(Hg\cdot HR)^*$ complex gives rise to the band fluorescence spectrum. With the reactive paraffins like propane the emission quantum yield is small, probably lower than 0.01, but with CH_4, C_2H_6, and $(CH_3)_4C$ it is substantially higher. From the shift of the position of band maxima with pressure the radiative lifetime of the excited complex is estimated to be 10^{-8}–10^{-9} sec. Collisional stabilization of the complex, step 7, apparently does not lead to complete deactivation because the decomposition quantum yields are independent of pressure.

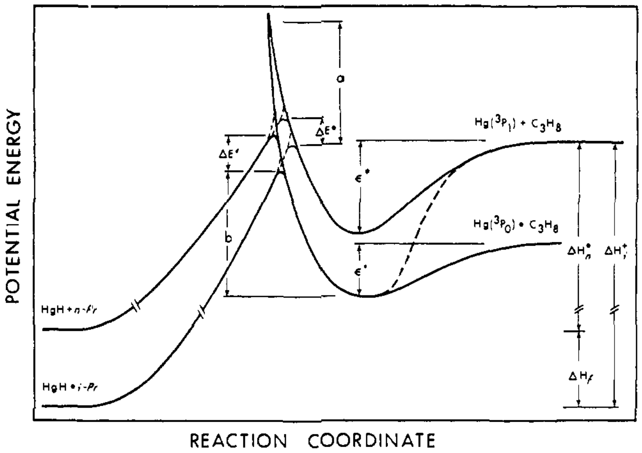

Figure 1. Schematic potential energy diagram for the interaction of Hg 6($^3P_1$) and Hg 6($^3P_0$) atoms with propane.

The corresponding steps for Hg^0 atoms are outlined in steps 9–15. It is assumed that the stability of the complex, ϵ^0, is somewhat diminished here because of the presumably lower polarizability of the Hg^0 atom. As a consequence, redissociation of the complex to reactants will be more facile, and because of the lower-lying position of the $^3P_0$ surface, the energy barrier for predissociation will be higher and the rate slower than from the $^3P_1$ surface. Thus the quenching rate constants of paraffins for Hg^0 atoms are predicted to be lower than for Hg* atoms, as observed experimentally. Also as a corollary of the relative locations of the relevant surfaces, ΔE^0, the energy difference of the crossing points to the repulsive curves correlating with the various modes of decomposition is larger than the corresponding value of ΔE^* for the $^3P_1$ curve and consequently Hg^0 atoms are predicted to be more discriminative with respect to C–H bond strength than Hg* atoms, a fact that has been borne out by recent experimental studies.[11]

Radiative transition from the $(Hg\cdot HR)^0$ complex, step 13, is less important than from the $(Hg\cdot HR)^*$ complex in spite of the slowness of the competing dissociative processes and can be attributed to the transition probability difference of the isolated atoms.

The inherent quantum deficiency of the decomposition reactions dictates an intersystem crossing, step 14, to the ground state, leading to the dispersion of the electronic energy without decomposition of the paraffin. The corresponding step from the $^3P_1$ curve would be less probable because of the location of the curves and also because of the higher efficiencies of the competing reactions.

Finally, the occurrence of a slow collisional deactivation, step 15, or reactivation to the $^3P_1$ manifold cannot be ruled out.

Turning now to the BEBO calculations, it is seen that the data in Table I predict the largest activation energy for the C–H bond in methane and the values decrease in the order of $C(CH_3)_4$, C_2H_6, C_3H_8, and i-C_4H_{10}. For the three states of mercury, ($^3P_0$), ($^3P_1$), and ($^1P_1$) the largest activation energy obtains for the $^3P_0$ state and the lowest for the $^1P_1$ state. In the reactions of the

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(15) A. C. Vikis and D. J. LeRoy, *Can. J. Chem.*, **50**, 595 (1972).
(16) In preparation for publication.

Table II. Kinetic Parameters for the Hydrogen Atom Transfer Reactions of O (^3P), Hg ($^3P_1$), and Hg ($^3P_0$) Atoms with Alkanes at 300°K

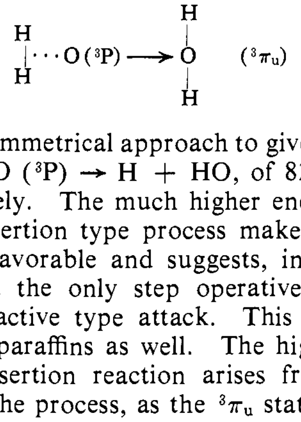
	O (^3P)			Hg ($^3P_1$)[d]	Hg ($^3P_0$)
Reagent	E_a, kcal mol^{-1}	Log A (cm^3 mol^{-1} sec^{-1})	Log k (cm^3 mol^{-1} sec^{-1})	Log k (cm^3 mol^{-1} sec^{-1})	Log k (cm^3 mol^{-1} sec^{-1})
H_2	10.2[a]	13.5	6.0	14.6	13.5,[e] 12.6[f]
CH_4	9.2[a]	13.3	7.5	12.2	9.6[e]
C_2H_6	6.1[a]	13.6	8.9	12.3	11.9,[g] 11.8,[h] 10.7,[e] 9.9[f]
C_3H_8	5.7[b]	13.70	9.7	13.5	12.4,[g] 12.6,[h] 11.4,[e] 10.9[f]
n-C_4H_{10}	5.1[c]	13.80	10.1	13.7	11.1[f]
neo-C_5H_{12}	5.8[c]	13.80	9.5	13.3	9.8[f]

[a] A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **50**, 2512 (1969); **47**, 1393 (1967). [b] K. Schofield, *Planet. Space Sci.*, **15**, 643 (1967). [c] J. T. Herron and R. H. Huie, *J. Phys. Chem.*, 73, 3327 (1969). [d] To be published. [e] Reference 10. [f] A. C. Vikis and H. C. Moser, *J. Chem. Phys.*, **53**, 1491 (1970). [g] S. Penzes, H. S. Sandhu, and O. P. Strausz, *Int. J. Chem., Kinet.*, **4**, 449 (1972). [h] J. M. Campbell, S. Penzes, H. S. Sandhu, and O. P. Strausz, *ibid.*, **3**, 175 (1971).

latter species the mechanism of the decomposition may follow a different path and instead, or in addition to abstraction, an insertion type process Hg ($^1P_1$) + HR → HHgR*, may prevail, followed by decomposition of the hot adduct.

Considering the computed energy differences for primary and secondary C–H bond cleavage $\Delta E \simeq 1.1$, 0.9, and 0.3 kcal/mol for $^3P_0$, $^3P_1$, and $^1P_1$ atoms, respectively, it is seen that the experimentally derived trend is correctly reproduced although the values and their spread are somewhat low. This discrepancy is partly due to the neglect of the triplet repulsive term which could not be meaningfully estimated in the calculation.[17]

It is common knowledge that divalent atoms and radicals in their triplet state can undergo hydrogen abstraction reactions with hydrogen donor molecules. Thus, the reactions of ground triplet state oxygen atoms, carbenes, nitrenes, and excited triplet state ketones such as benzophenone, etc., have been extensively investigated with a variety of donor molecules. However, absolute rate parameters for these reactions are sparse and in the case of paraffins are available only for reactions with oxygen atoms. It is interesting to compare the reactivity of O (^3P) with that of Hg^0 and Hg* atoms. The relevant data are compiled in Table II. In general, the variation of reactivity with the molecular structure of the paraffin is similar for the three reagents and, probably because of the higher exothermicity of their reactions, the mercury atoms are considerably more reactive and consequently somewhat less discriminative than oxygen atoms with respect to C–H bond strength. The rate constant values for a given reagent are determined largely by the strength of the C–H bond and the BEBO calculations correctly predict the observed trends. For oxygen atoms, as expected, the experimental and predicted rates of reaction with hydrogen are lower than with paraffins. For Hg^0 and Hg* atoms, however, the rate constants are extremely high, lying in the order of the gas kinetic collision frequency, indicating an abrupt change in the mechanism. Recently Bader and Gangi[18] reported a theoretical study of the O (^3P) + H_2 reaction within the framework of molecular orbital theory. They computed activation energies for the symmetrical approach of the oxygen atom to form the lowest linear triplet state of water



$$\begin{matrix} H \\ | \\ H \end{matrix} \cdots O(^3P) \longrightarrow \begin{matrix} H \\ | \\ O \\ | \\ H \end{matrix} \quad (^3\pi_u)$$

and for the asymmetrical approach to give radical products, H–H···O (^3P) → H + HO, of 82 and 35 kcal/mol, respectively. The much higher energy barrier of the former insertion type process makes this step energetically unfavorable and suggests, in line with experiment, that the only step operative is the asymmetrical abstractive type attack. This is most likely the case with paraffins as well. The high energy barrier of the insertion reaction arises from the endothermicity of the process, as the $^3\pi_u$ state of water lies some 50 kcal/mol above the H_2 + O (^3P) reactant state. In the case of mercury on the other hand, the corresponding triplet state of the H_2Hg molecule is probably below the reactant state H_2 + Hg*, lowering the activation energy of the insertion

$$H_2 + Hg^* \longrightarrow {}^3(HHgH)$$

below that of the abstraction step.

$$H\text{-}H + Hg^* \longrightarrow H + HHg$$

In fact the activation energy of the insertion must be close to zero to account for the high efficiency of the process. Thus it appears that in going from paraffins to hydrogen the mechanism is identical in the case of oxygen atoms, but changes from abstraction to insertion with mercury, causing an abrupt increase in the expected rate constant. The insertion mechanism for the H_2 + Hg* reaction has originally been postulated by Callear and McGurk[19] on the basis of flash spectroscopic observations.

In conclusion, it is proposed that the triplet mercury sensitized decomposition of paraffins is a hydrogen abstraction process of the divalent, paramagnetic, excited mercury atom, and should be treated as such. That the reagent is an electronically excited species does not present conceptual difficulties in formulating such a process since precedents for such reactions are not uncommon. Thus it is well established that a significant primary step in the triplet mercury photosensitized de-

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(17) It should be pointed out here that the experimentally determined *n*-propyl to isopropyl yield ratio of *ca.* unity in the $^1P_1$ atom sensitization of propane (R. A. Holroyd and T. E. Pierce, *J. Phys. Chem.*, 68, 1392 (1964)) does not necessarily reflect the reactivity of $^1P_1$ atom because parallel to decomposition, relaxation of $^1P_1$ atoms to the triplet manifold followed by the ^3P sensitization of propane may occur. The upper limit of triplet atom participation is estimated to be ~36%.

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composition of alkyl halides is chlorine atom abstraction by the excited mercury atom.

$$RCl + Hg^* \longrightarrow R + HgCl$$

In the triplet cadmium photosensitized decomposition of paraffins the major primary step is C–H bond cleavage which becomes energetically feasible only if the process is a true hydrogen transfer.

$$RH + Cd^* \longrightarrow R + CdH$$

The formation of CdH in the course of the reaction can be readily detected spectroscopically.[20,21] Finally, hydrogen abstraction by excited triplet reagents such as $^3(n,\pi^*)$ benzophenone, acetone, etc., are well known in organic photochemistry.

In considering the general facets of excited-state chemistry, one notes the enhanced stability of the reaction complex arising from the higher polarizability of the excited atom. Also, the presence of the larger number of available reaction channels renders the excited chemistry more complex than that of ground-state systems and causes a pronounced departure from simple second-order kinetics on the microscopic scale.

Decomposition of the paraffin occurs *via* a predissociative step, and interconversion of Hg* and Hg^0 atoms *via* internal conversion of the reaction complex in competition with radiative decay from the (RH·Hg)* surface. Internal conversion, resulting in spin–orbit relaxation, requires a considerably higher molecular compression and shorter RH···Hg* bond distance than predissociation, leading to cleavage of the R–HHg bond. This indicates that in the reaction complex the total angular momentum vector remains well defined and consequently the reaction model, as outlined here incorporating only two reaction surfaces, is probably an oversimplified representation of the reaction system. Moreover, the *A* factors of the overall quenching reactions are high and therefore symmetry restrictions on the internal process cannot be severe. If this is the case then the noncrossing rule,[22] that two states belonging to the same irreducible representation always avoid crossing, would also require a different surface for each internal process.

The observed pressure dependence of the molecular band fluorescence maxima would seem to suggest that at high pressure vibrational relaxation of the reaction complex may be occurring. This, however, should alter the relative yields of the various primary steps, for which no experimental evidence exists at present.

Further experimental and theoretical studies are currently in progress and will be reported at a later date.

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Inner-Orbital Photoelectron Spectroscopy of the Alkali Metal Halides, Perchlorates, Phosphates, and Pyrophosphates

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Abstract: Binding energies for Li "1s," Na "1s," K "$2p_{3/2}$," Rb "3d," Cs "$3d_{5/2}$," F "1s," Cl "2p," Br "3d," I "$3d_{5/2}$," O "1s," and P "2p" orbitals, when appropriate, were measured on crystalline alkali metal halides, perchlorates, phosphates, and pyrophosphates. The range of the observed binding energies was found to be narrow (within 2 eV) for each of the alkali metals in the various salts studied, whereas a somewhat greater range (*ca.* 3 eV) was found for the halogens in the alkali metal halides. The range of phosphorus binding energies in the phosphates and pyrophosphates was also small (*ca.* 1 eV and 2 eV, respectively). The variations in the experimental binding energies of the alkali metal halide salts were found to parallel the variations in the respective orbital energies calculated for the corresponding gaseous diatomic molecules in a near-limit Hartree–Fock approximation.

Since the main thrust in the study of solid materials by inner-orbital photoelectron spectroscopy (ESCA)[2,3] has been on covalently bonded molecules, it seemed desirable to extend this technique to a systematically selected array of anhydrous crystalline salts. Traditionally, the alkali metal halides have been considered as typical ionic lattice structures, so we have focused on these compounds. The perchlorates and orthophosphates were included since they represent the common MO_4 type of anion. In addition, the pyrophosphates were run in comparison with the orthophosphates.

Experimental Section

The inner-electron binding energies reported herein were obtained from a Varian induced-electron-emission (IEE) spectrometer[4] which

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