if the lifetime $\tau_{\rm m}$ of the metastable state of benzene is known. Many of the experimental values needed to carry out these interesting calculations are not known with certainty. The experiments presently reported permitted the elaboration of a plausible scheme for the phenomenon studied and point the way to further research in this area.

A scheme involving self-quenching of the sensitizer could explain the above results without supposing deactivation to and transfer from the lowlying metastable state. However, observations in this laboratory as well as elsewhere³ indicate that self-quenching in benzene is relatively unimportant.

It is also of interest to note that because β naphthylamine appears in its lowest vibrational states, in the process under consideration, the system behaves (from the point of view of electronic energy transfer) in the same manner as a liquid or solid system where vibrational energy is dissipated rapidly. In a recent publication on sensitized phosphorescence in organic solutions at low temperatures, Terenin and Ermolaev⁴ represent the dependence of naphthalene phosphorescence sensitized by benzaldehyde at fixed concentrations of the phosphorescer by

where

$$I_a$$
 = phosphorescence intensity of naphthalene at concn.
"c" of benzaldehyde, which absorbs the exciting
radiation

 $I_{\rm c} = I_{\rm lim} (1 - e^{-ac})$

 $I_{\rm lim}$ = the saturation level of intensity

a = constant

This equation is algebraically equivalent to our equation 6, for a system where the fluorescer is completely transparent to the exciting radiation.

(3) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York, N. Y., 1949, p. 265.

(4) A. Terenin and V. Ermolaev, Trans. Faraday Soc., 52, 1042 (1956).



Fig. 4.—Experimental test of equation 6, for two values of β -naphthylamine pressure.

It is of interest to note what other information or applications are latent in this relatively simple type of experiment.

Having an experimental value of K_s , the rate constant for transfer of electronic energy and assuming no activation energy for the transfer process, one can calculate an effective cross-section. Crosssections for reactions of electronically excited species are known to differ from those for normal species but *a priori* calculations are not possible using current methods.

Finally, it is an observation in radiation chemistry that small amounts of aromatics stabilize certain compounds which otherwise decompose easily when subjected to the radiation. This stabilization effect is explained by employing energy transfer processes to the aromatic. Since the transfer process from benzene can be very efficient, the reverse process, using benzene as an energy sink, also can take place efficiently under certain conditions.

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THE IGNITION OF EXPLOSIVES BY RADIATION¹

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In the known experiments of Norrish² and Porter² the radiation, which is emitted as very high energy within milliseconds by suitable electric discharges, serves to dissociate gases, such as chlorine, into atoms or radicals. In these cases the absorbed energy is consumed in making possible one or several chemical processes; the system reacts exclusively with the absorbed energy, even if it returns to the original state in some cases by dark reactions afterwards. In this case the absorbed energy is therefore stored as chemical energy; the system operates just as a plant during the photosynthesis. Principally different is the behavior of a mixture of chlorine and hydrogen; for chlorohydrogen can be caused to detonate by sufficiently large quantities of absorbable radiation and is converted to hydrogen chloride even by radiation of lower intensity with a high quantum yield (of the order of $\varphi = 10^{\circ}$), because in this "endothermic system" chain reactions may occur, as Bodenstein atoms. They react according to $Cl + H_2 \rightarrow HCl + H$, $H + Cl_2 \rightarrow HCl + Cl$ with continuous production of HCl molecules and with continuous alternating delivery of H and Cl atoms until either the chain is broken by trapping of the atoms (mutually or by reaction with foreign substances), or until the entire mixture completes the reaction explosively, *i.e.*, thermically.

In Zürich we tried for some time to find the answer to the question whether solid compounds of endothermic character like chlorohydrogengas mixture can also be caused to detonate by a

(1) J. Eggert, Physik. Bl., 10, 549 (1954).

(2) (a) R. G. W. Norrish, Z. Elektrochem., 56, 705, 712 (1952);
(b) G. Porter and F. J. Wright, *ibid.*, 56, 782 (1952).

sufficiently large amount of radiation. Principally such systems should be found among the explosives, particularly among those which in other respects, especially mechanically, also possess a high degree of sensitivity. The first representative which we found was nitrogen iodide (NH_3NI_3) which as brown-black powder can be ignited by the radiation

J. Eggert

TABLE I

Detonation temperature in °C. (IV), electrical energy of the discharge in w.s. (V), irradiated energy in w.s./cm.² (VI) for electronic flashes of 0.8 ms. duration as minimal values of the radiation to produce detonation for some endothermic compounds (I and II). Compounds in powder form, originally at room temperature.

I (Compound)	II (Formula)	III (Appearance)	IV (D.T.)	Dis- charge energy	Irr. energy i.e.
Nitrogen iodide	NI3NH3	Brown-black	50	19	0.16
Silver nitride	$Ag_{3}N$	Black	100	24	0.20
Cuprous acetylide	Cu_2C_2	Brown-black	120	75	0.63
Silver acetylide (alk. ppt.)	Ag_2C_2	White	165	95	0.79
Silver acetylide (neutral ppt.)	$Ag_2C_2 \cdot AgNO_3$	Yellowish white	225	230	1.9
Mercurous acetylide	Hg_2C_2	Light gray	280	>350	>2.8
Mercuric acetylide	HgC_2	White	260	180	1.5
Silver azide	AgN₃	White	250	310	${f 2}$. 6
Lead azide	$Pb(N_3)_2$	Yellowish-white	350	240	2.0
Mercuric azide	$Hg(N_3)_2$	White	270	310	2.6
Silver fulminate	AgONC	White	170	250	2.1
Mercuric fulminate	$Hg(ONC)_2$	Light gray	190	200	1.65
Diazobenzene nitrate	$C_6H_5N_3O_3$	Yellowish	90	110	0.92
Diazobenzene perchlorate	$C_6H_5N_2ClO_4$	White	155	110	0.92
<i>p</i> -Diazodiphenylamine perchlorate	$C_{12}H_{10}N_8ClO_4$	Yellow	170	95	0.79
Ammonium perchromate	(NH ₄) ₃ CrO ₈	Red-brown	90	135	1.10
	I (Compound) Nitrogen iodide Silver nitride Cuprous acetylide Silver acetylide (alk. ppt.) Silver acetylide (neutral ppt.) Mercurous acetylide Mercuric acetylide Silver azide Lead azide Lead azide Mercuric azide Silver fulminate Diazobenzene nitrate Diazobenzene perchlorate p-Diazodiphenylamine perchlorate Ammonium perchromate	$\begin{array}{ccc} I \\ (Compound) \\ \hline \\ \begin{tabular}{lllllllllllllllllllllllllllllllllll$	$\begin{array}{cccc} I & II & III \\ (Compound) & (Formula) & (Appearance) \\ Nitrogen iodide & NI_3NH_3 & Brown-black \\ Silver nitride & Ag_3N & Black \\ Cuprous acetylide & Cu_2C_2 & Brown-black \\ Silver acetylide (alk. ppt.) & Ag_2C_2 & White \\ Silver acetylide (neutral ppt.) & Ag_2C_2 & White \\ Silver acetylide (neutral ppt.) & Ag_2C_2 & Ught gray \\ Mercuric acetylide & Hg_2C_2 & Ught gray \\ Mercuric acetylide & AgN_8 & White \\ Lead azide & Pb(N_3)_2 & Yellowish-white \\ Mercuric fulminate & AgONC & White \\ Silver fulminate & Hg(ONC)_2 & Light gray \\ Mercuric fulminate & C_6H_6N_3O_3 & Yellowish \\ Mercuric fulminate & C_6H_6N_3O_3 & Yellowish \\ Mercuric fulminate & C_6H_6N_2ClO_4 & White \\ Diazobenzene perchlorate & C_{12}H_{10}N_6ClO_4 & Yellow \\ Ammonium perchromate & (NH_4)_3CrO_8 & Red-brown \\ \end{array}$	$\begin{array}{cccc} I & II & III & IV \\ (Compound) & (Formula) & (Appearance) & (D.T.) \\ Nitrogen iodide & NI_3NH_3 & Brown-black & 50 \\ Silver nitride & Ag_3N & Black & 100 \\ Cuprous acetylide & Cu_2C_2 & Brown-black & 120 \\ Silver acetylide (alk. ppt.) & Ag_2C_2 & White & 165 \\ Silver acetylide (neutral ppt.) & Ag_2C_2 & Mite & 165 \\ Silver acetylide & Hg_2C_2 & Light gray & 280 \\ Mercuric acetylide & Hg_2C_2 & White & 260 \\ Silver azide & AgN_8 & White & 250 \\ Lead azide & Pb(N_3)_2 & Yellowish-white & 350 \\ Mercuric fulminate & Hg(ONC)_2 & Light gray & 190 \\ Diazobenzene perchlorate & C_8H_8N_2ClO_4 & White & 155 \\ p-Diazodiphenylamine perchlorate & (NH_4)_3CrO_8 & Red-brown & 90 \\ \end{array}$	$\begin{array}{c c} I \\ (Compound) \\ \hline H \\ (Compound) \\ \hline H \\ (Compound) \\ \hline H \\ (Formula) \\ \hline $

of electronic flashes with remarkable reproducibility with regard to the incident minimal energy. In sunlight, however, the nitrogen iodide undergoes a slow decomposition because the radiation intensity furnished by the sunlight is insufficient to trigger the detonation.

During the course of our investigation we found a series of other compounds having the same property (Table I). The magnitude of the detonation energy (cols. V and VI) indicate that highly colored compounds (col. III) are more "sensitive" than those which are white (colorless) and therefore absorb less of the incident energy. Column IV also indicates that there is a distinct correlation with the detonation temperature,



Fig. 1.—Pictorial record of the detonation of nitrogen iodide initiated by an open spark, $27 \ \mu s$. after release of the initiation spark. The separation of the sound wave emanating from the explosion from the smoke is plainly visible. The also visible sound waves from the spark are kept away from the sample by the glass plate.

i.e., that temperature at which the explosive detonates in the dark (on rapid heating); high detonation temperatures correspond to high detonation energies; we shall discuss this point later.

Let us consider first the case of nitrogen iodide which my co-worker B. Meerkämper³ has investigated.

According to older experiments it could be expected that the compound would decompose according to

$NH_3NI_3 + h\nu \longrightarrow N_2 + 3HI$

The hydrogen iodide formed reacts further according to

 $3HI + 3NH_3NI_3 \longrightarrow 4NH_4I + 1.5N_2 + 4.5I_3$

so that the quantum yield should be at least $\varphi =$ 4, provided that this value is not still greater because of the energy liberated during the decomposition (60 kcal./mole). Surprisingly it was found that the value $\varphi = 4$ is far from being reached, even with intense, but for detonation inadequate irradiation, but amounts only to $\varphi = 0.15$ to maximally $\varphi = 0.6$ (at 21° and 15 torr.) according to the conditions. The lower values were observed in an ammonia atmosphere, the higher ones in air. In the presence of NH₃ therefore the major part of the primarily formed HI is trapped; it cannot react farther and we observe the low yield $\varphi = 1/4$; 0.6 = 0.15. On the other hand, this figure shows that every 7th quantum only leads to a decomposition of the nitrogen iodide, while the others are converted into heat without taking part photochemically or thermally in the decomposition of the nitrogen iodide. So the absorbed radiation can act either purely photochemically or it can cause the decomposition of the substance by local heat-ing, *i.e.*, thermally. This is supported, *inter alia*, by the fact that the decomposition on irradiation has a temperature coefficient exceeding 1 ($\tau =$ 2.3) for the range from 18.5 to 25°). In order to decide this question, Berchtold⁴ carried out the

(3) B. Meerkämper, Thesis No. 2262, ETH Zürich, 1953; Z. Elektrochem., 58, 387 (1954). irradiation of nitrogen iodide with the compound in concentrated aqueous ammonia so that the HI secondary reaction as well as thermal effects were practically excluded. Actually the quantum yield decreased from $\varphi = 0.15$ to 0.06 and the temperature coefficient from $\tau = 2.3$ to 1.1. This indicates that the "slow" decomposition of the dry nitrogen iodide on irradiation with high intensity light sources is largely photothermal and to a minor part, only about 5–10%, of photochemical nature. Consequently we observed a pronounced ignitability for dry nitrogen iodide, a lower one for water-moistened, and none at all for ammonia-wet compound. The small purely photochemical conversion with "throttled" secondary reaction is insufficient to initiate the detonation.

The detonation of the hydrogen iodide itself also furnished various illuminating observations by means of high speed cinematography. Reference to Fig. 1 anticipates the objection that the initiation may not be caused by radiation but by a mechanical impulse (pressure wave). The deduction from Fig. 1, of course, does not exclude that the substance may be ignited by a pressure wave as was shown by special experiments.

The initiation of the other compounds listed in Table I was purely photothermal. The following experiment proved this. The explosive was first ignited at room temperature (20°) by light flash, and the electrical energy of the discharge tube required was entered in a diagram in the manner of Fig. 2. The minimal energy (in w.s.) required for the initiation was determined, after the compound had been raised to a higher temperature as rapidly as possible. Figure 2 shows the curve obtained in this manner for silver acetylide (precipitated from acid solution). We see that the initiation energy decreases with increasing temperature of the compound and converges toward zero at the (dark) ignition temperature of 225°. Consequently the radiation has to supply only the amount of energy which is required to heat the compound surface until it reaches the ignition temperature (col. IV of Table I). Analogous observations were made with nitrogen iodide³ and lead azide⁵ (Figs. 3 and 4).

There are several reasons why, on the other hand, the initiation energies J for the compounds listed in Table I (all irradiated at room temperature) are in loose relationship only to the corresponding ignition temperatures t (col. IV), so that there is no simple function J = f(t) in this case. Firstly, the spectral absorptivities of the compounds differ so that they take up different fractions of the incident energy; secondly, the compounds have different thermal capacities, and finally they differ in heat conductivity. All these properties, however, determine the heating of the surface layer to the ignition temperature, so that we can hardly expect another pattern than the series of dots given in Fig. 5 for the value pairs recorded in Table I for initiation energy (col. V) and initiation temperature (col. IV). The distribution of the dots shows



Fig. 2.—The energy of the flash lamp required for the ignition of silver acetylide $(AgC_2, AgNO_3)$ in relation to the initial temperature of the sample.



Fig. 3.—The energy of the flash lamp required for the ignition of nitrogen iodide (NH_3NI_3) in relation to the initial temperature of the sample.



Fig. 4.—The energy of the flash lamp required for the ignition of lead azide, $Pb(N_3)_2$, in relation to the initial temperature of the sample.

that the effect of the ignition temperature is dominant over the other factors mentioned.

This, however, holds true for a certain duration of the radiation only, which in our case amounted to 0.8 ms., and is valid for a certain layer thickness of the compounds investigated. In order to study these two factors we used silver nitride (Ag₃N) as test object. Like the other compounds this substance can be prepared as a loose powder, but

⁽⁴⁾ J. Berchtold, Thesis No. 2376, ETH Zürich, 1954.

⁽⁵⁾ F. Eggert and J. Berchtold, Naturwiss., 40, 55 (1953).



Fig. 5.—Graphic representation of the value pairs: initiation energy I.E. and initiation temperature D.T. from Table I for some endothermic compounds (same numbering).



Fig. 6.—The minimum radiation (w.s./cm.²) required for the ignition of silver nitride mirrors in relation to the layer thickness of the mirror (μ) . The detonation does not spread to the left of the arrow.



Fig. 7.—Flash print of a line original on a silver nitride paper. The black Ag_2N coating has been destroyed by the detonation in the bright areas so that the paper base is visible through a silver haze; in the dark areas the Ag_2N coating has gradually changed to silver.



Fig. 8.—Effect of the exposure time (ms.) on the minimal radiation energy $(w.s./cm.^2)$ required for the ignition of silver nitride.

under suitable experimental conditions it can also be precipitated on smooth surfaces as uniformly dense mirror-like deposits of variable thickness.

We noticed that silver nitride as powder layer and as mirror deposit of about 1 μ thickness (on glass) requires the same irradiation of at least 0.2 w.s./cm.² for ignition. If we systematically decrease the thickness, the ignition sensitivity of the mirror decreases at first slowly (as indicated by the curve of Fig. 6), then rapidly, as is evident from the minimal values for the radiation intensity (required to initiate a detonation) which increases steeply toward the lower thicknesses. During the course of these experiments we made the surprising observation that mirrors with a thickness exceeding 0.15μ (arrow in Fig. 6) detonate, even if only a small fraction of the surface is irradiated; the detonation initiated at the irradiated spot does not spread to non-irradiated areas if the thickness of the layer sinks below 0.15 μ . Apparently the layer in this case loses too much energy to the surroundings (support) to maintain the propagation of the detonation wave.

This effect could be used to prepare copies of line originals by flash illumination on such mechanically quite insensitive layers, as the example of Fig. 7 shows. The silver nitride remaining on the print, which corresponds to the dark areas of the original, after some time spontaneously changes to silver by decomposition, and therefore neither development nor fixation is required for this "dry" printing process which yields positives from positives with a resolution of 10 lines per mm. So far technical reasons make the process unsuitable for practical purposes at this moment.

In a second series of experiments Berchtold investigated the effect of the duration of the flash to the minimal amount of radiation required for the initiation and got the curve of Fig. 8, which was obtained with silver nitride powder. We see that the quantity of radiation directed at the substance can be the smaller the shorter its available time. Whereas, for example, the energy of 0.02 w.s./cm.² absorbed in the layer surface after an irradiation time of some milliseconds has time to drain off to colder areas and remain without effect, it accumulates in one hundreth of this time to such an extent that the ignition temperature is reached and detonation occurs. On the other hand, Meerkämper could prove by high speed cinematographic analysis that the detonation of nitrogen iodide starts long before the light flash ends, and therefore only a fraction of the incident energy is used for the detonation.

A number of phenomena could be reported about the other compounds listed in Table I, for example, that silver azide AgN₃ (no. 8), which by normal exposure is decomposed with formation of silver and nitrogen, shows the surprisingly low quantum yield of $\varphi = 0.1$ only, although silver bromide and silver chloride, the compounds used in photography, yield the value $\varphi = 1^6$ in spite of their

(6) J. Eggert and R. Zemp, Z. Naturforsch., 86, 389 (1953); also R. Zemp, thesis No. 2150, ETH Zürich, 1953.

similarity to Ag_8N . However, we shall point out in conclusion that the ignitability of thin aluminum foils (of 0.5 μ thickness) in the presence of oxygen is based on a photothermal process also. It has been shown that the radiation required for the ignition of the aluminum in an O_2 atmosphere amounts within certain limits to about 2 w.s./cm.². If we assume the average spectral absorption of the used radiation to be 8%, a rise in temperature of about 1200° is indicated by the heat capacity of the system, and this, of course, suffices for the ignition of the aluminum. That in this case a photothermal effect is involved can be concluded also from the fact that the radiation sufficient to cause ignition can be reduced to less than half if the absorption of the aluminum foil is increased by a thin coating of carbon black.

A METHOD FOR EVALUATING RATE CONSTANTS IN THE JABLONSKI MODEL OF EXCITED SPECIES IN RIGID GLASSES¹

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A method is presented for calculating kinetic rate constants for processes that occur according to the Jablonski model of electronically excited dye molecules in rigid glasses. Non-radiative transitions from excited to ground states are considered in addition to the radiative transitions usually considered. Since the rate constants are found by use of data on fluorescence, α -phosphorescence and β -phosphorescence, the method is limited in use to temperatures above about 180°K.

Introduction

The energy level model proposed by Jablonski to explain the qualitative features of observed emissions from excited molecules in rigid media² has been used with considerable success in semiquantitative studies of such systems, and in some instances theoretical justifications for the assumptions regarding the natures of the energy levels have been found.³⁻⁶ Until the appearance of the work by Koizumi and Kato,^{7,8} however, no solution to the kinetic problem had been published in which non-radiative transitions were permitted to occur from both excited electronic levels. Their work, which was concerned with identifying the excited level involved in quenching with gaseous agents, led to the most general solution of the kinetic problem presently available.

In the present work, a procedure is presented whereby the individual rate constants for processes occurring in the Jablonski model can be computed with the aid of specific emission data. Use is made of Koizumi and Kato's time-dependent solutions in a slightly modified form, and of steady-state solutions. It is assumed that the only temperature

(1) Supported in part by the Office of Ordnance Research on Contract No. DA-23-072-ORD-581.

(2) A. Jablonski, Z. Physik, 94, 38 (1935).

(3) G. N. Lewis and M. Kasha, J. Am. Chem. Soc., 66, 2100 (1944).

(4) G. N. Lewis and M. Calvin, ibid., 67, 1232 (1945).

(5) G. N. Lewis, M. Calvin and M. Kasha, J. Chem. Phys., 17, 804 (1949).

(6) D. S. McClure, ibid., 17, 905 (1949).

(7) M. Koizumi and S. Kato, ibid., 21, 2088 (1953).

(8) M. Koizumi and S. Kato, J. Inst. Polytechnics (Osaka, Japan), 4, 149 (1953).

dependent process is the one by which molecules are thermally activated from the triplet to the singlet level. In some instances such an assumption may not be valid,⁹ but it was shown to be satisfactory for at least one system in a semiquantitative investigation by Lewis, Lipkin and Magel.¹⁰

The Use of Emission Data to Solve for Rate Constants.—The time-dependent solutions given by Koizumi and Kato are written in terms of the symbols appearing in Fig. 1 as

$$N_{\rm B} = Q[r_1^{-1}(r_1 + R_{\rm T})e^{r_1t} - r_2^{-1}(r_2 + R_{\rm T})e^{r_2t}] (r_2 - r_1)^{-1} (1)$$

and

$$N_{\rm T} = k_3 Q [r_1^{-1} e^{r_1 t} - r_2^{-1} e^{r_2 t}] (r_2 - r_1)^{-1}$$
(2)

in which $R_{\rm S}$ is the sum $k_1+k_2+k_3$ and $R_{\rm T}$ is the sum $k_4+k_5+k_6$. The quantities r_1 and r_2 are roots of the auxiliary equations for the second-order differential equation involved in the solution of the rate equations. Steady-state solutions are

$$N_{\rm S} = R_{\rm T} Q (R_{\rm S} R_{\rm T} - k_3 k_6)^{-1} \tag{3}$$

and

$$N_{\rm T} = k_3 Q (R_{\rm S} R_{\rm T} - k_3 k_6)^{-1} \tag{4}$$

In eq. 1, 2, 3 and 4 all non-radiative processes from a given excited state to the ground level are assigned a single rate constant which is the sum of the rate constants for the several non-radiative processes possible from that state. In this regard the

(9) E. J. Bowen and D. M. Stebbins, J. Chem. Soc., 360 (1957).

(10) G. N. Lewis, D. Lipkin and T. T. Magel, J. Am. Chem. Soc..
 63, 3005 (1941).