Application of Time-Resolved Infrared Spectroscopy to the Determination of Absolute Rate Constants for CI + C_2H_6 and CI + C_2H_5CI

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Time-resolved infrared spectroscopy (TRISP) has been used to determine at 700 Torr and 298 K the absolute rate constants of reactions (1) $Cl + C_2H_6 = C_2H_5 + HCl [k_1 = 7.05 (\pm 1.4) \times 10^{-11} cm^3/molecule s]$ and (2) $Cl + C_2H_5Cl = C_2H_4Cl$ + HCl $[k_2 = 6.8 (\pm 1.4) \times 10^{-12} cm^3/molecule s]$. Pulsed UV laser photolysis of Cl_2 in flowing mixtures of Cl_2 , C_2H_6 (or C_2H_5Cl), and air initiated the reaction. Absolute rate constants were measured by observing the rate of HCl production using this pulsed, broad-band IR technique for time delays from 50 ns to 10 μ s after the photolysis laser pulse. Because chain propagation occurs via reactions (4) $C_2H_5 + Cl_2 = C_2H_5Cl + Cl$ or (6) $C_2H_4Cl + Cl_2 = C_2H_4Cl_2 + Cl$, corrections for these reactions were included in the absolute rate calculations. A determination of the rate constant of reaction 6 relative to reaction 5, $C_2H_4Cl + O_2 = C_2H_4ClO_2$, was required to calculate k_2 . The ratio k_6/k_5 was measured at 700 Torr by continuous UV photolysis of Cl_2 , O_2 , and C_2H_5Cl mixtures in a static reactor using the relative rate technique. Values of $k_6/k_5 = 0.42$ (±0.06) and 0.63 (±0.15) were obtained for 1-chloroethyl and 2-chloroethyl radicals, respectively. The measured value of k_1 agrees with previous low-pressure (<10 Torr) determinations verifying that reaction 1 is pressure independent.

Introduction

The kinetics of the reactions of Cl atoms with hydrocarbons have been studied extensively, and one of the most important of these reactions is with ethane:

$$Cl + C_2H_6 = C_2H_5 + HCl$$
 (1)

This reaction and that of methane are benchmarks against which Cl atom reaction rate constants have been measured in relative rate studies. While many of these relative rate experiments have been carried out near atmospheric pressure, the absolute measurements of reaction 1 have been performed at pressures below 10 Torr, $^{1-4}$ with the exception of one measurement at 100 Torr of helium.² No pressure variation has been observed below 10 Torr, and the small variation observed in helium between 15 and 100 Torr at high initial Cl atom densities has been ascribed to side reactions. Thus, it is likely that this reaction is pressure independent, as expected. However, because of the importance of reaction 1, we have undertaken a measurement of its rate constant as well as that of reaction 2, at atmospheric pressure

$$Cl + C_2H_5Cl = C_2H_4Cl + HCl$$
 (2)

during initial tests of our time-resolved infrared spectroscopy (TRISP) apparatus. TRISP provides a broad-band pulse of infrared radiation which can be used to probe both the reactants and products of very fast (50 ns) chemical reactions. These rate constant measurements are carried out using pulsed photolysis of flowing mixtures containing Cl_2 , C_2H_6 (or C_2H_5Cl), and air. The formation of HCl is followed as a function of reaction time to determine the absolute rate constants.

Experiment

The TRISP apparatus and technique have been described in detail.⁵ Briefly, visible radiation near 430 nm from a broad-band, pulsed dye laser is used to generate pulsed, broad-band infrared (IR) radiation (2700–3200 cm⁻¹) by stimulated electronic Raman scattering (SERS) in a rubidium vapor heat pipe. The IR probes a reacting mixture flowing through a three-pass cell in which a photochemical reaction has been initiated by pulsed laser radiation.

The consumption of reactants and generation of products can thus be observed on time scales as short as the laser pulse width (<20 ns). After passing through the cell, the IR is shifted into the visible wavelength range by four-wave mixing in a potassium heat pipe, synchronously pumped by a narrow-band, pulsed dye laser, to facilitate detection of the IR spectrum. The visible radiation, which contains the IR signature, is dispersed by a monochromator and imaged on a silicon-intensified target vidicon controlled by an optical multichannel analyzer.

The reaction cell consists of a quartz flow tube (2.2 cm i.d. \times 6 cm length) with BaF₂ windows attached to each end. A flowing mixture of Cl₂, hydrocarbon, and air is passed through the cell at a total flow rate of 14 L/min, which provides complete cell purging between the 3-Hz photolysis pulses of a XeF excimer laser at 351 nm. The air flow rate is controlled by a Tylan mass flow controller, while the Cl₂ and hydrocarbon flow rates are measured by calibrated rotameters. In addition, samples of the flowing reactant mixture are withdrawn downstream of the reactor for gas chromatographic (GC) analysis to verify the hydrocarbon concentration. The total pressure in the reactor is maintained at 700 Torr by adjusting a throttling valve leading to a vacuum pump. The range of reactant partial pressures studied was Cl₂ = 21.5-45 Torr, C₂H₆ = 1.75-6.5 Torr, and C₂H₅Cl = 2.25-7.0 Torr.

The pulsed 351-nm radiation (135 mJ at the cell), which photolyzes the molecular chlorine, is focused onto the side of the reactor in a band that overlaps as uniformly as possible the axially directed IR probe radiation. During a set of runs taken on one day, the energy of the photolysis laser varied by less than 5%. The IR probe pulse reaches the reaction cell at a predetermined variable delay time (50 ns to 1 ms) following the onset of the photolysis reaction to measure the gas composition as a function of reaction time.

Results

Each experimental determination of k_1 and k_2 was carried out on a single day to minimize variability in the HCl determinations. The principal source of day-to-day variability in the HCl measurements was changes in the instrumental resolution caused by the alignment changes required for optimizing the signal-to-noise ratio at the beginning of each day's runs. Such resolution changes produced approximately $\pm 15\%$ changes in the peak optical density of the HCl lines during calibration runs on different days. No realignment was performed during a series of runs on a single day

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TABLE I: Measured [HCI], for All Experiments

| | | | | [HCl], Tori | r | | | $[\mathbf{R}]_{ak} d$ |
|----------------|----------------------------------------|--------------------------------------|------------------|-------------|-------|----------------------------|----------------------------------------|----------------------------------|
| delay time, µs | [Cl ₂] ₀ , Torr | [R] ₀ , ^a Torr | $\overline{A^b}$ | В | C | [HCl] _{av} , Torr | [HCl] _∞ , ^c Torr | Torr cm ³ /molecule s |
| Ethane | | | | | | | | |
| 0.065 | 45.0 | 6.53 | 0.220 | 0.230 | 0.250 | 0.233 | | |
| 0.130 | | | 0.415 | 0.375 | 0.370 | 0.387 | | (54.7) ^e |
| 0.250 | | | 0.455 | 0.465 | 0.445 | 0.459 | 0.513 | 50.8×10^{-11} |
| 0.100 | 45.0 | 4.30 | 0.260 | 0.165 | 0.215 | 0.213 | | |
| 0.300 | | | 0.455 | 0.460 | 0.450 | 0.455 | | (22.0) |
| 3.000 | | | 0.660 | 0.590 | 0.630 | 0.627 | 0.630 | 22.1×10^{-11} |
| 0.100 | 45.0 | 3.83 | 0.225 | 0.160 | 0.165 | 0.183 | | |
| 0.250 | | | 0.325 | 0.280 | 0.310 | 0.305 | | |
| 0.500 | | | 0.475 | 0.450 | 0.410 | 0.445 | | (26.1) |
| 1.000 | | | 0.435 | 0.455 | 0.455 | 0.448 | 0.463 | 25.1×10^{-11} |
| 0.200 | 21.0 | 1.83 | 0.100 | 0.130 | 0.118 | 0.116 | | |
| 0.700 | | | 0.227 | 0.180 | 0.205 | 0.204 | | (15.7) |
| 10.000 | | | 0.227 | 0.205 | 0.235 | 0.222 | 0.222 | 15.4×10^{-11} |
| 0.200 | 45.0 | 1.76 | 0.220 | 0.190 | 0.200 | 0.203 | | |
| 0.600 | | | 0.320 | 0.335 | 0.300 | 0.317 | | (14.3) |
| 2.000 | | | 0.480 | 0.440 | 0.465 | 0.462 | 0.449 | 13.9×10^{-11} |
| Ethyl Chloride | | | | | | | | |
| 0.300 | 46.5 | 7.04 | 0.155 | 0.160 | 0.135 | 0.150 | | |
| 0.900 | | | 0.280 | 0.300 | 0.280 | 0.287 | | |
| 2.500 | | | 0.348 | 0.380 | 0.410 | 0.379 | 0.384 | 58.4×10^{-12} |
| 1.000 | 46.5 | 3.92 | 0.205 | 0.220 | 0.242 | 0.222 | | |
| 2.500 | | | 0.365 | 0.455 | 0.460 | 0.427 | | |
| 10.000 | | | 0.475 | 0.450 | 0.503 | 0.476 | 0.490 | 23.9×10^{-12} |
| 0.500 | 46.5 | 3.82 | 0.095 | 0.115 | 0.110 | 0.107 | | |
| 1.300 | | | 0.250 | 0.215 | 0.205 | 0.223 | | |
| 10.000 | | | 0.426 | 0.385 | 0.395 | 0.402 | 0.430 | 22.5×10^{-12} |
| 1.000 | 46.5 | 2.24 | 0.155 | 0.125 | 0.140 | 0.140 | | |
| 3.000 | | | 0.280 | 0.245 | 0.275 | 0.267 | | |
| 10.000 | | | 0.465 | 0.410 | 0.365 | 0.413 | 0.421 | 13.7×10^{-12} |

^a Hydrocarbon partial pressure measured by GC. Each group of data was taken on one day. Total pressure of each mixture was raised to 700 Torr with air. ^b HCl partial pressure from three HCl transitions (A = 2798.8, B = 2821.5, C = 2843.6 cm⁻¹). ^c [HCl]_w calculated from fit of HCl data to expression X (see text). ^d Product of partial pressure of hydrocarbon with rate constant obtained from fit of expression X to each data set (see text). ^eNumbers in parentheses are the final preferred values used in Figure 2. They have been corrected for small errors in eq W' as discussed in the text.

in order to avoid resolution changes.

The IR spectrum obtained for each time delay represents the sum of 6000-8000 laser pulses for both I (reacting mixture) and I_0 (empty cell) signals, requiring approximately 2 h/data point. Data were acquired at three to four delay times (t) for each mixture tested, with the measured [HCl], spanning the range 35% to >90% of the value at infinite time. The HCl concentration at each delay time was determined from the peak absorbances of the m = -2, -3, and -4 lines of the P branch. Absolute HCl concentrations were obtained from a calibration curve of the IR optical density for each line. The calibration curves were generated by flowing through the reaction cell a 5.4% HCl in nitrogen mixture (Matheson Gas Products), which was diluted with air to 700 Torr. The HCl pressures in these flowing mixtures spanned the range covered in the experiments (0.15-1 Torr). A typical set of spectra for one experimental condition is presented in Figure 1. Delay times after the photolysis pulse are 100, 250, 500, and 1000 ns; growth of HCl with increasing time is evident. The HCl concentration deduced from each of the transitions and their average are presented in Table I as a function of delay time for each experimental condition.

The major reactions that occur in the presence of ethane following the essentially instantaneous Cl_2 photolysis are

$$Cl + C_2H_6 = HCl + C_2H_5$$
 (1)

$$C_2H_5 + O_2 = C_2H_5O_2$$
(3)

$$C_2H_5 + Cl_2 = C_2H_5Cl + Cl$$
 (4)

Using this reaction scheme, the rate of reaction 1 can be measured by following the rise of HCl. Reaction 3 is essentially a termination reaction on the time scales of our experiments and does not lead to additional HCl production. If reaction 3 were the sole sink for ethyl radicals, the HCl density after complete consumption of the atomic chlorine would be equal to the initial chlorine atom



Figure 1. Infrared absorption spectra of HCl obtained at four probe delay times (100, 250, 500, and 1000 ns) after the photolysis laser pulse. $[C_2H_6]_0 = 3.83$ Torr, $[Cl_2]_0 = 45$ Torr, air = 651 Torr. The successive spectra are offset from one another by approximately 0.02 optical density units to avoid overlap.

concentration. Reaction 4, however, provides chain propagation, and the final HCl density will actually be equal to the sum of the initial chlorine atom concentration plus the amount of ethyl chloride generated during the reaction. Ethyl chloride cannot be measured in these experiments because its IR spectrum is overlapped by the much stronger high-concentration ethane bands (see ref 5). Therefore, a correction is required in order to deduce the rate constant of reaction 1 from the time dependence of the HCl density.

On the basis of reactions 1, 3, and 4, an analytic equation may be derived which describes the time dependence of the HCl density $([HCl]_t = \text{density at time } t \text{ and } [HCl]_{\infty} = \text{density at infinite time}),$ if the $[O_2]$, $[Cl_2]$, and $[C_2H_6]$ remain constant during the reaction. Under the above assumption

$$d[HCl]/dt = k_1[Cl][C_2H_6]_0$$
 (W)

$$[Cl] = [Cl]_0 - A[HCl] \qquad (W')$$

$$A = 1/\{1 + (k_4[Cl_2]/k_3[O_2])\}$$

Noting that

$$[\mathrm{HCl}]_{\infty} = [\mathrm{Cl}]_0 / A$$

and substituting into eq W, we obtain

$$d[HCl]/dt = Ak_1[C_2H_6]_0[[HCl]_{\infty} - [HCl]]$$

This equation can be solved exactly to obtain the relationship between the observed HCl profile and the rate constant of reaction 1:

$$[HCl]_{t} = [HCl]_{\infty} \{1 - \exp(-k_{1}A[C_{2}H_{6}]_{0}t)\}$$

In fact, $[Cl_2]$ and $[O_2]$ are constant to within 2% under the reaction conditions studied, but $[C_2H_6]$ decreases by 7-25% during the reaction depending upon its initial value. A satisfactory correction for this decrease which still permits the use of the analytic solution can be made by replacing $[C_2H_6]_0$ with its average value between times = 0 and t:

$$[C_2H_6]_{av} = ([C_2H_6]_0 - 0.5[HCl]_t)$$

This yields

[]

$$HCl]_{t} = [HCl]_{\infty} \{1 - \exp(-k_{1}A[C_{2}H_{6}]_{av}t)\}$$
(X)

Term A results from the chain reaction and can be calculated from the known [Cl₂], [O₂], and the rate constant ratio, $k_4/k_3 = 2.0 \pm 0.12$, which has been measured at 700 Torr in air.⁶ Each set of data was analyzed by fitting expression X to all [HCl], values for one data set with $k_1[C_2H_6]_0$ and [HCl]_∞ as adjustable parameters. The fitted values of these parameters are also included in Table I for each data set. The fitted values of $k_1[C_2H_6]_0$ are sensitive only to the shape of the HCl vs time curve and not to the absolute HCl concentration. As an example, increasing all [HCl] values in one data set by 20% during the fitting process increases the calculated [HCl]_∞ by 20% but changes the $k_1[C_2H_6]_0$ by only 0.5%. Thus, the above mentioned 15% uncertainty in the absolute HCl concentration will not affect the calculated values of k_1 .

Equation W' will be valid only when the time constant of HCl formation is long relative to the time constant of $[C_2H_5]$ consumption by reactions 3 and 4. For the high $[C_2H_6]_0$ concentrations, an additional small correction was required in the calculation of k_1 from the above fits. To estimate the magnitude of this correction, we generated HCl profiles from reactions 1, 3, and 4 using a chemical kinetics program which simultaneously solves these partial differential equations. These test profiles were generated at reaction times and initial conditions similar to those for each data set in Table I. These HCl profiles were subsequently fitted to expression X in order to obtain a value of k_1 which could be compared to the value used in the chemical kinetics solver which generated the test profiles. The values of k_1 obtained from expression X were lower by 2-8%, and these corrections were used to give the preferred $[C_2H_6]_0k_1$ values presented in parentheses in Table I.

Two additional reactions might affect the results of these experiments:

$$Cl + O_2 + M = ClO_2 + M$$
 (7)

$$C_1 + C_2 H_5 = C_2 H_4 + HC_1$$
 (8)

Reaction 7 is slow relative to reaction 1 under our conditions ($k_7 = 4 \times 10^{-14} \text{ cm}^3/\text{molecule s}$) and its equilibrium constant predicts that $\text{ClO}_2/\text{Cl} = 0.03.^7$ Thus, this reaction should have little effect



Figure 2. Plot of the product $k[R]_0$ versus $[R]_0$ for determination of k_1 (=7.05 ± 1.4 × 10⁻¹¹ cm³/molecule s) and k_2 (=6.8 ± 1.4 × 10⁻¹² cm³/molecule s).

on the calculated rate constant. Two very different estimates have been made of the rate constant of reaction 8: $k_8 = 2 \times 10^{-10}$,⁸ or 1.2×10^{-11} cm³/molecule s.¹ The faster rate constant combined with the known value of k_3 (=9 × 10⁻¹² cm³/molecule s)⁶ indicates that the HCl generated by reaction 8 would cause an overestimation of less than 4% in the value of k_1 as calculated from our HCl data, far smaller than its uncertainty. Experiments performed with C₂H₆ at two different initial Cl₂ concentrations (see Table I) produced [Cl]₀ values which differ by a factor of 2. The rate constants derived from these two conditions are identical, lending support to the above statement that the effect of reaction 8 is negligible.

A similar analysis can be carried out for ethyl chloride by substituting reactions 2, 5, and 6 into expression (X):

$$Cl + C_2H_5Cl = HCl + C_2H_4Cl$$
 (2)

$$C_2H_4Cl + O_2 = C_2H_4ClO_2$$
 (5)

$$C_2H_4Cl + Cl_2 = C_2H_4Cl_2 + Cl$$
 (6)

The ratio k_6/k_5 has not been measured previously, and therefore a value of k_6/k_5 was determined for each of the two chloroethyl isomers formed in reaction 2 using the relative rate technique described in ref 6. To make these measurements, static mixtures of Cl₂, C₂H₅Cl, and O₂ were irradiated with black lights in a Pyrex reactor. The consumption of ethyl chloride and fromation of 1,1and 1,2-dichloroethane were observed by gas chromatography. The value of k_6/k_5 for the 1-chloroethyl radical determined from these experiments was 0.42 ± 0.06 and for the 2-chloroethyl radical 0.63 ± 0.15 in which the error limits are 2σ of the mean. No pressure dependence was observed for k_6/k_5 between 100 and 700 Torr to within experimental error. Because formation of the 1-chloroethyl radical constitutes 83% of reaction 2,9 the value 0.42 was used in the calculation of the parameter A in expression X. The values of $k_1[C_2H_5Cl]_0$ and $[HCl]_{\infty}$ obtained by fits of the HCl data to X are also presented in Table I. No correction for the slight error in eq W' was applied to these data. Absolute rate constants for neither reaction 5 nor reaction 6 have been measured. However, if we make the reasonable assumption that $k_5 = k_3$, then the substantially slower rate of reaction 2 relative to 1 will make the correction negligible for ethyl chloride.

The rate constants k_1 and k_2 were determined by a linear least-squares fit of $k_1[C_2H_6]_0$ (corrected) to $[C_2H_6]_0$ or of k_2 - $[C_2H_5Cl]_0$ to $[C_2H_5Cl]_0$ using the data in Table I. Figure 2 presents these plots and the least-squares fits, which yield the following rate constants and 2σ error limits:

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 $k_1 = 7.05 \ (\pm 1.4) \times 10^{-11} \ \mathrm{cm}^3/\mathrm{molecule s}$

 $k_2 = 6.8 \ (\pm 1.4) \times 10^{-12} \ \mathrm{cm}^3/\mathrm{molecule s}$

The value of k_1 can be compared with previous absolute measurements at 298 K and pressures below 10 Torr: 6.1 (±0.1);1 6.0 (± 0.7) ;² 5.93 (± 0.45) ;³ 5.5 $(\pm 0.6)^4 \times 10^{-11}$ cm³/molecule s. Our rate constant is 20% larger than the average of these four measurements, well within the stated error limits, and is only 15% larger than the measurement¹ with the smallest stated error limits that was carried out at the lowest pressure. Therefore, our value of k_1 agrees with all previous measurements to within experimental uncertainty, verifying that there is no pressure dependence to this reaction from 10⁻⁵ to 700 Torr. Only one other absolute measurement has been made of k_2 . At 298 K and 100 Torr of argon, Wine and Semmes¹⁰ obtain $k_2 = 8.04 \ (\pm 0.57) \times 10^{-12} \ \mathrm{cm}^3$ molecule s, which again agrees with the value from our experiments to well within the error limits.

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Perthivi Radicals, Trisulfide Radical Ions, and Sulfate Formation. A Combined Photolysis and Radiolysis Study on Redox Processes with Organic DI- and Trisulfides

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The formation of perthial and thial radicals has been studied in a combined photochemical and radiation chemical investigation of the di- and trisulfides of penicillamine and cysteine, together with glutathione disulfide, cystamine dihydrochloride, and dithiodiglycolic acid in aqueous solution. The highest RSS' yields are found from the trisulfides with little difference between PenSSSPen and CySSSCy in the case of photolysis, but with a (4-5):1 ratio in favor in PenSS* over CySS* upon radiation chemically induced processes. Thiyl radicals are the other major species formed. The RSS'/RS' ratio changes significantly depending on the nature of the di- or trisulfide and the method of radical generation employed. Perthiyl radicals are found to be moderately good oxidants, weaker though than thiyl radicals, and readily react with molecular oxygen in an addition process. The following absolute rate constants have been measured: $k(\text{PenSS}^{\bullet} + \text{ascorbate}) = (4.1 \pm 1.0) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{PenSS}^{\bullet} + O_2) = (5.1 \pm 1.0) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Probably the most interesting finding about perthip radicals is that inorganic SO_4^{2-} is formed in their reaction with molecular oxygen. The mechanism of sulfate formation is suggested to proceed via the perthioperoxyl radical, RSSOO*, structural rearrangement of this transient into the corresponding sulfonyl-type radical, RSSO₂[•], addition of oxygen to the latter to yield a sulfonyl peroxyl, RSSO₂OO[•], followed by a bimolecular radical-radical reaction of these peroxyl radicals (in analogy to the fate of peroxyl radicals in general) leading to RSSO₃[•]. Cleavage of SO₃ from RSSO₃[•] and hydrolysis would then result in SO₄²⁻. Reduction of trisulfides yields (RSSSR)⁻⁻ radical anions which decay into either RSS[•] + RS⁻ (preferred pathway in case of PenSSSPen reduction; k{PenSSSPen + e_{aq}^{-} } = 2.0 × 10¹⁰ M⁻¹ s^{-1} , k[PenSSSPen + CO₂⁻⁻] = 2.3 × 10⁸ M⁻¹ s⁻¹), or RS[•] + RS⁻ (preferred pathway in case of CySSSCy reduction). Trisulfide radical anions could directly be identified in the case of the cysteine compound with (CySSSCy). absorbing at 425 nm and exhibiting a half-life of ca 4 μ s. Radical cations (PenSSSPen)⁺ are indicated in the oxidation of penicillamine trisulfide.

Introduction

The disulfide bond provided by cystine plays a major role in the structure and function of many proteins.¹ Numerous studies have shown that organic disulfides are easily oxidized through free radicals like ${}^{\circ}OH$, ${}^{2-4}$ reactive oxygen species like $O_3{}^5$ and ${}^{1}O_2{}^{6,7}$ and many other oxidizing radicals.^{8,9} Such reactions thus constitute potent ways of protein inactivation. Moreover, disulfides have been shown to suffer bond breakage by one-electron re-duction^{10,11} or photochemical processes.^{12,13} While splitting of the sulfur-sulfur bond, with generation of RS* radicals, appears to be the major route of radical-induced disulfide destruction, carbon-sulfur bond rupture may also occur, particularly when tertiary carbon substituents are attached to the disulfide bridge. The latter would lead to the perthiyl radical, RSS[•], which constitutes the sulfur analogues of the well-known and chemically rather well-characterized peroxyl radicals, ROO^{•.14}

Whereas research has focused particularly on the reactivity of oxygen-centered radical species in biological environment, e.g., with respect to the pathology of many diseases,^{15,16} surprisingly minor attention was paid for a long period to the biochemical role

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