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# KINETIC DETERMINATION OF THE METAL—METAL BOND DISSOCIATION ENERGY IN BIS(DICARBONYL $\eta^5$-CYCLOPENTADIENYLIRON)

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## Summary

The iron—iron bond energy in $[C_5H_5Fe(CO)_2]_2$ (I) has been determined by measuring the rate of disproportionation of the monoacetyl complex $(AcC_5H_4)$-$(C_5H_5)Fe_2(CO)_4$ (II) to I and $[AcC_5H_4Fe(CO)_2]_2$ (III). The reaction follows first order kinetics in benzene solution in the temperature range of 60—100°C with activation parameters calculated as: $\Delta H^{\ddagger} = 26.9 \pm 2.7$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 2.0 \pm 3.2$ cal mol$^{-1}$ deg$^{-1}$.

## Introduction

Despite current interest in metal—metal bonding in organometallic complexes of the transition elements and the widespread occurrence of such bonding [1,2], relatively few well established data for metal—metal bond strengths are available.

Bond dissociation energies have been determined mass spectrometrically for $Mn_2(CO)_{10}$ [3,4,6,7], $Tc_2(CO)_{10}$ [7], $Re_2(CO)_{10}$ [4,7], $MnRe(CO)_{10}$ [4] and for $Co_2(CO)_8$ [5,6], and these energies for $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ have been shown to be in accord with enthalpy values for the equilibrium: $M_2(CO)_{2n} \rightleftharpoons 2\ M(CO)_n$ [6], obtained from gas phase measurements.

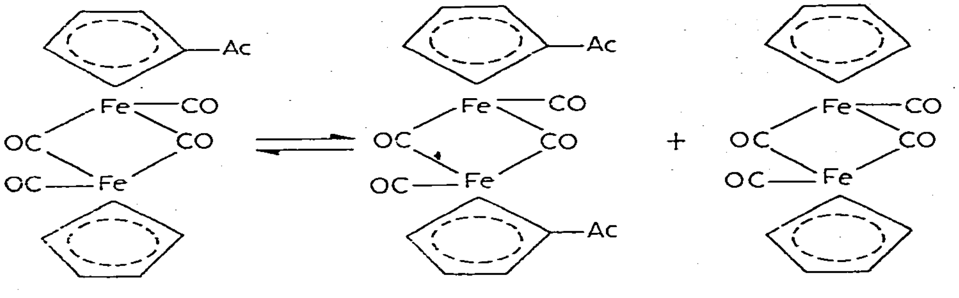
Where comparable, activation enthalpies for metal—metal bond homolysis, derived from kinetic measurements of substitution and decomposition reactions [8—10], are generally found to be 10—15 kcal mol$^{-1}$ higher than bond dissociation energies derived by electron impact studies. The discrepancies between these figures have been ascribed to either kinetic or excitation energies of the radicals produced by electron impact [4,8,10], or to a substantial enthalpy of activation for radical recombination [8b,c].

More recently, ESR measurements have established the equilibrium of $[\eta^3$-$C_3H_5Fe(CO)_3]_2$ with its monomer and have yielded values for the enthalpy and entropy of this reaction [11].

The present paper reports a simple kinetic method by which the activation energy for metal—metal bond dissociation in $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (I) may be determined. The reaction studied is mechanistically simple and is uncomplicated by side reactions. Moreover the method may in principle be extended to the corresponding Ru and Os complexes, to related Group VI complexes, and to heterometallic cyclopentadienyl complexes of these and other transition metals.

## Results and discussion

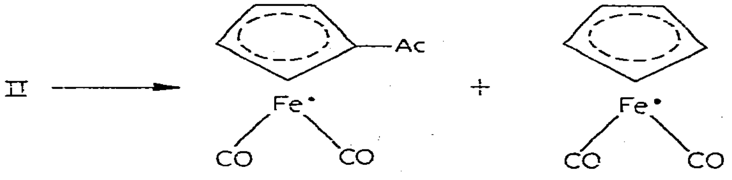
In the course of earlier work [12], we carried out the Friedel—Crafts acetylation of I, and noted that the monoacetyl derivative II underwent disproportionation during recrystallization to give mixtures of I, II and the diacetyl dimer (III) *.



(II) (III) (I)

(1)

Such a change is best depicted as proceeding through recombination of the organometallic radicals IV and V, derived from thermal dissociation of II. The equilibrium postulated in eq. 2 is well precedented by a number of dinuclear



(IV) (V)

(2)

complexes including $Mn_2(CO)_{10}$ [6], $Co_2(CO)_8$ [6], $Fe_2(CO)_8I_2$ [14], $[\eta^3\text{-}C_3H_5Fe(CO)_2]_2$ [15], and $[\eta^5\text{-}C_5H_5Fe(NO)CH_3]_2$ [16], which have been shown to be in thermal equilibrium with their corresponding monomeric radicals. Kinetic evidence has also been provided for the rate-limiting homolysis of metal—metal bonds in the thermal substitution and decomposition reactions of $Mn_2(CO)_{10}$ [8].

More recently it has been shown that homolysis of metal—metal bonds may also be achieved photochemically [17—19]. Among these, the organometallic radical V has been characterized by ESR and spin trapping experiments [18]. In view of these results, it is not improbable that photochemically induced insertion of olefins and acetylenes into metal—metal bonds [20] of binary transition

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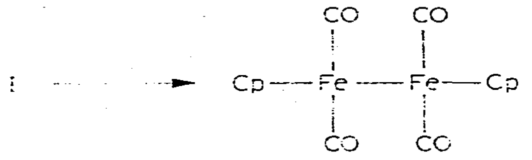
* A similar disproportionation of dicarbonylmethylcyclopentadienyliron dimer in the presence of I has recently been reported [13].

metal—main group metal complexes takes place through an initial metal—metal bond homolysis.

The observation, summarized by eq. 1, provided the means for determining the activation energies associated with homolysis of I, II and III. Although this energy necessarily includes a term corresponding to the conversion of the carbonyl-bridged tautomer I to the non-bridged form (eq. 3), energy parameters for this change have been estimated for *cis* and *trans* forms of I from IR and NMR studies [21,22].



$$\mathrm{I} \longrightarrow \mathrm{Cp{-}}\underset{\mathrm{CO}}{\overset{\mathrm{CO}}{\mathrm{Fe}}}\mathrm{{-}}\underset{\mathrm{CO}}{\overset{\mathrm{CO}}{\mathrm{Fe}}}\mathrm{{-}Cp} \qquad (3)$$

(VI)

### *The kinetic expression*

Derivation of the integrated kinetic expression (eq. 4) for the rate of dissociation of I, based on an analysis of the competitive, reversible dissociative processes shown in eq. 5—7 is given in detail in the experimental section.

$$k_{-2}t = [-(2+r)/(2K+r)]\ln[K(\mathrm{AB})_i - (\mathrm{AA})(2K+r)] + [(2+r)/(2K+r)]\ln K(\mathrm{AB})_i \qquad (4)$$

$$\mathrm{AB} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A} + \mathrm{B} \qquad (5)$$

$$2\,\mathrm{A} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{AA} \qquad (6)$$

$$2\,\mathrm{B} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{BB} \qquad (7)$$

In these expressions, AA, AB and BB represent the dimeric complexes I, II, and III respectively, and A and B represent the radicals V and IV respectively. The dissociation of the dinuclear complexes is assumed to occur by an uncatalyzed unimolecular process, and the imposition of steady-state conditions in the derivation of eq. 4 requires that the rates of radical recombination be very rapid compared with these dissociative reactions. The rates of recombination of the radicals A and B may be expected to be very nearly equal, as may the rates of dissociation of the symmetrical dinuclear complexes I and III. Consequently, the constant $r$, which is a measure of the steady-state ratio (V/IV) is taken as unity. The Fe—Fe bond dissociation energy of II would, however, be expected to be greater than that of I and III. This is confirmed by a measurement of the equilibrium constant ($K_e$) for the equilibria 5—7. At 80°C the value of this constant is very nearly half of the statistical value of 0.25. In expression 4, the constant $K$ represents the ratio of rate constants ($k_1/k_{-2}$) for the dissociation of II and I.

The value of 0.350 for $K$, determined from $K_e$, is equivalent to an activation energy for the dissociation of II which is approximately 0.80 kcal mole$^{-1}$ greater than that for I.

Initial attempts to follow the formation of I and III or the loss of II by PMR spectrometry were unsuccessful. The close chemical shifts for the unsubstituted cyclopentadienyl ring proton resonances in I and II in a variety of solvents made separate integration of the absorptions difficult, and the use of shift reagents did not markedly affect the spectra.

We turned, therefore, to following the formation of I from II by chromatographic separation of the reaction components, coupled with quantitative infrared determination of I, using the bridging carbonyl absorption at 1790 cm$^{-1}$. Although this procedure is somewhat tedious, blank runs with pure I or known mixtures of I and II showed that the loss of I in these manipulations was less than 3%.

Plots of the rate expression (eq. 4) are shown in Fig. 1 for temperatures between 60 and 100° C. Those kinetic runs carried out between 70 and 100° C were followed over at least four half lives, while those at 60 and 65° C were followed over two half lives. Good linearity was shown throughout. Rate data are summarized in Table 1.

A computerized least squares fitting of the six points for the rate constant ($k_{-2}$) between the temperatures 60—100° C gives activation parameters: $\Delta H^{\ddagger} = 26.9 \pm 2.7$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 2.0 \pm 3.2$ cal mol$^{-1}$ deg$^{-1}$, for the dissociation of I. Since the enthalpy term for the conversion of I to the non-bridged isomer (eq. 3) has been estimated as 4 kcal mol$^{-1}$, an activation enthalpy of approximately 23 kcal mol$^{-1}$ may be associated with the metal—metal cleavage step.

For comparison, literature values of bond dissociation energies determined by electron impact ionization and of enthalpies of activation for metal—metal

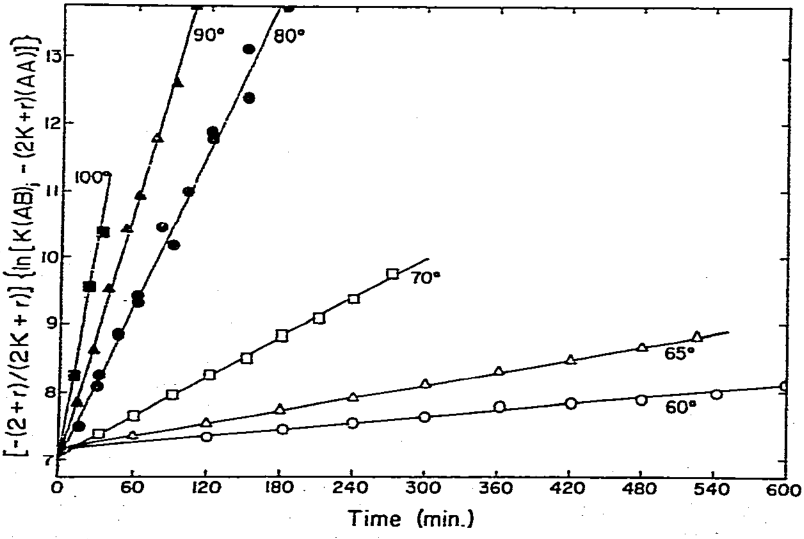


Fig. 1. Plot of rate data for the thermal disproportionation of monoacetyl dicarbonyl cyclopentadienyliron dimer (II). $r = 1$, $K = 0.350$.

TABLE 1

RATE DATA FOR DISSOCIATION OF I IN BENZENE SOLUTION

| Temperature (°C) | Rate ($k_{-2} \times 10^3$ min$^{-1}$) |
|---|---|
| 60 | 1.70 ± 0.13 |
| 65 | 3.20 ± 0.03 |
| 70 | 9.86 ± 0.49 |
| 80 [a] | 39.0 ± 1.7 |
| 90 | 66.7 ± 3.0 |
| 100 | 141.3 ± 15 |

[a] Average of two runs.

bond homolysis from kinetic measurements are summarized in Table 2. As indicated earlier, the lower dissociation energies for $Mn_2(CO)_{10}$, derived from mass spectrometric measurements have been attributed to kinetic or excitation energies, or to an activation energy associated with radical recombination. However, the agreement between electron impact bond energies [3,4,7] and the enthalpy values for gas phase dimer ⇌ monomer equilibria for $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ [6] suggest that kinetic or excitation energies do not appreciably affect the mass spectrometric measurements for these complexes. Activation energies for radical recombination have been calculated from kinetic studies, to be small for $Co(CO)_3PBu_3$ [10], but substantial (12 kcal mol$^{-1}$) for $Mn(CO)_5$ radicals [8b]. Such activation has been attributed to a higher stability for a $D_{3h}$ rather than a $C_{4v}$

TABLE 2

METAL—METAL BOND ENERGIES

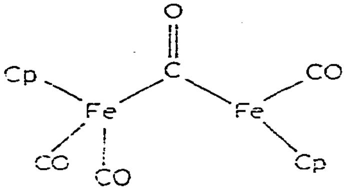
| Complex | Bond dissociation energies [a] | | Activation enthalpies [b] | |
|---|---|---|---|---|
| | $D$(M—M) (kcal mol$^{-1}$) | Ref. | For bond homolysis | Ref. |
| $Mn_2CO)_{10}$ | 18.9 | 3 | 36.6 | 8 |
| | 22.1 | 4 | 36.8 ± 0.4 | 8b |
| | 21 ± 3 [c] | 6 | 37.0 ± 0.3 | 8c |
| | 34 ± 13 [d] | 29 | 16 ± 2 | f |
| | 24.9 ± 0.7 | 7 | | |
| $Tc_2(CO)_{10}$ | 42.4 ± 0.4 | 7 | | |
| $Re_2(CO)_{10}$ | 51.2 | 4 | 38.6 ± 0.4 | 9 |
| | 44.7 ± 1 | 7 | | |
| $ReMn(CO)_{10}$ | 61.6 | 4 | | |
| | 50.2 ± 2 | 7 | | |
| $Co_2(CO)_8$ | 13 ± 3 [c] | 6 | | |
| | 11.5 ± 4.6 | 5 | | |
| $[CO(CO)_3PBu_3]_2$ | | | 26.4 ± 0.7 [e] | 10 |
| $[C_5H_5Fe(CO)_2]_2$ | | | 23<br>32 [e] | this work |

[a] By electron impact ionization studies. [b] From kinetics of reaction with $PPh_3$, $I_2$ or of thermal decomposition. [c] From gas phase equilibria studies. [d] From heat of sublimation of $Mn_2(CO)_{10}$, other thermodynamical data and spectroscopically determined valency promotion energies. [e] From kinetics of reaction with $SnBr_2$. [f] Calculated by Faucett, Poë and Sharma [8b] from data of ref. 30.

configuration for $Mn(CO)_5$ radicals [8b]. On the other hand spectroscopic evidence appears to support a $C_{4v}$ configuration for both $Mn(CO)_5$ and $Re(CO)_5$ formed by cocondensation of metal vapor and CO at low temperatures [23,24], and energy differences between $C_{4v}$ and $D_{3h}$ for $d^7$ $M(CO)_5$ fragments have been calculated as small and in favor of $C_{4v}$ [25].

For the Group VII carbonyls, $M_2(CO)_{10}$, dissociation energies appear to increase sharply in the sequence Mn < Tc < Re. These relative energies have been shown [7] to correlate well with force constant calculations based on Raman spectra [26]. It would be of interest to see if the same trend is observed for the Group VIII $[C_5H_5M(CO)_2]_2$ complexes, since M—M force constants for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [27] show a similar trend.

An estimation of 32 kcal $mol^{-1}$ has recently been made for the Fe—Fe bond energy, based on rates of insertion of $SnBr_2$ into the metal—metal bond of I [28]. Reaction kinetics were shown to conform to a two step process involving rate-limiting formation of a reactive intermediate. This was formulated as the dinuclear species VII, with a single carbonyl bridge and no iron—iron bond, although little if any clear precedent exists for such an intermediate.



(VII)

Moreover, Barrett and Sun [28] assume that the activation energy for breaking one bridging carbonyl unit in I would be half the value associated with the cleavage of two such units in the conversion of I—VI (estimated to be 13 ± 2 kcal $mol^{-1}$) [22]. The iron—iron bond energy is taken as the difference between the activation energy for the formation of VII (38 kcal $mol^{-1}$) and this energy. It is clear that this calculation must be regarded with some reservation since it derives from a questionable partitioning of energy terms between hypothetical processes.

## Experimental

All reactions and manipulations were carried out in a nitrogen atmosphere. Solvents were thoroughly degassed by purging with nitrogen and then distilling from benzophenone ketyl. Melting points were determined in nitrogen-filled capillary tubes. IR spectra were recorded on a Perkin—Elmer model 457 spectrophotometer (GM-16395). NMR spectra were recorded on a model A-60A spectrometer (GM-13183). Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

### *Acetylation of dicarbonyl $\eta^5$-cyclopentadienyliron dimer*

A solution of dicarbonyl $\eta^5$-cyclopentadienyliron dimer (I) (6.00 g, 17.0 mmol) in 200 ml of methylene chloride was cooled to —20°C. A slow stream of boron trifluoride was passed into the solution while acetic anhydride (5.0 ml, 53 mmol) was added dropwise over a period of 10 min. The solution was stirred at 0° for 3 h, then poured into 600 ml of an aqueous, saturated sodium carbonate solution. Workup gave a dark purple solid, which was taken up in 150 ml of methylene chloride/benzene solution (2 : 3) and chromatographed on 450 g of activity 2, Camag, neutral alumina. Elution with benzene gave unreacted starting material as the first band. This was followed by a broad brown band, which on elution with ether/benzene (1 : 3) gave 830 mg (37%) of monoacetylated dimer (II), m.p. 150°C (dec.); IR ($CHCl_3$) 2015, 1964, 1778, 1672 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 5.15 (s, 5, Cp), 5.13 (t, 2 $J$ 2 Hz, $\beta$-Cp), 4.81 (t, 2, $J$ 2 Hz, $\alpha$-Cp), 7.47 ppm (s, 3, Ac). (Found: C, 48.11; H, 3.11. $C_{16}H_{12}Fe_2O_5$ calcd.: C, 48.48; H, 3.03%.)

A small amount of diacetylated dimer (III), m.p. 156°C (dec.); IR ($CHCl_3$) 2023, 1971, 1784, 1678 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 5.07 (t, 2, $J$ 2 Hz, $\beta$-Cp), 4.71 (t, 2, $J$ 2 Hz, $\alpha$-Cp), 7.47 ppm (s, 6, Ac). (Found, 49.31; H, 3.48; Fe, 25.87. $C_{18}H_{14}Fe_2O_6$ calcd.: C, 49.30; H, 3.19; Fe, 25.57%.)

### *Kinetic runs*

The monoacetylated dimer II was purified by chromatography on activity II alumina with benzene/ether solutions. It was then vacuum dried at room temperature and stored at —10°C. NMR spectral analysis did not indicate the presence of I. Control experiments showed that 1% of I could be detected in solutions of II by this method.

A solution, prepared from 1.000 g of II in 50.00 ml of benzene, was placed in a 100 ml two necked flask, equipped with a nitrogen inlet. The solution was heated at temperatures between 60 and 100°C in a constant temperature bath (±0.1°C). Aliquots were withdrawn periodically with a 5.00 ml transfer pipette attached to a syringe, and quenched by discharging into flasks, cooled to —80°C. The aliquots were chromatographed on 40 g of activity 3 alumina with benzene. Well defined bands of I were collected, solvent was removed and the concentration of I was determined by IR spectral analysis.

### *IR spectral analysis*

The aliquots were taken up in 4.00 ml of tetrahydrofuran and the IR spectrum of these solutions were recorded over a 1840—1700 $cm^{-1}$ range, on a Perkin—Elmer 457 spectrophotometer, using a 2.5 abscissa expansion scale. Absorbancy values for the bridging carbonyl peak at 1790 $cm^{-1}$ were obtained by base line-peak analysis and were averaged over 5 scans. Concentrations of I were calculated from a Beers law plot, previously determined over a range of 20 to 5 mg of I in 4.00 ml of THF, which was shown to be linear and to pass through the origin.

### *Evaluation of experimental error*

Solutions prepared from 1.000 g of I in 50.00 ml of benzene (50.51 mmol $l^{-1}$) were heated at 80°C in the apparatus used for the kinetic runs. Eight aliquotes (5.00 ml) were withdrawn over a period of four hours and processed chromatographically. The weights of I recovered were determined by IR analysis and showed a loss of less than 0.3% between aliquots.

In a second set of experiments, known weights of I (5 to 20 mg) were combined with 50 mg of II. These mixtures were chromatographed under the conditions described above, and the concentration of I was determined by IR spectral analysis. Weight recovery of I averaged 98 ± 1% of initial weight.

*Determination of $K_e$*

We define the equilibrium constant $K_e$:

$$K_e = (AA)_e(BB)_e/(AB)_e^2$$

where $(AA)_e$, $(BB)_e$ and $(AB)_e$ are the equilibrium concentrations of dimer I, diacetylated dimer III and monoacetylated dimer II, respectively.

Since $(AA)_e = (BB)_e$ and $(AB)_e = (AB)_i - [(AA)_e + (BB)_e]$, where $(AB)_i$ is the initial concentration of monoacetylated dimer II, we have:

$$K_e = (AA)_e^2/[(AB)_i - 2\,(AA)_e]^2$$

The equilibrium constant, $K_e$, was determined at 80° C, employing the data for two separate kinetic runs which were allowed to proceed through 10 half lives (180 min). The average value of $(AA)_e$ was 10.4 ± 0.1 mmol $l^{-1}$, from which

$$K_e = 0.123 \pm 0.015$$

is calculated, assuming a 5% error in the determination of $(AA)_e$.

*Derivation of the integrated kinetic expression*

For the reactions:

$$AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B \tag{5}$$

$$2\,A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AA \tag{6}$$

$$2\,B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} BB \tag{7}$$

where (AA), (AB) and (BB) are instantaneous concentrations of I, II and III respectively and (A) and (B) are concentrations of dicarbonylcyclopentadienyliron (V) and dicarbonylacetylcyclopentadienyliron (IV) radicals respectively.

Under conditions of steady state:

$$d(A)/dt = k_1(AB) - k_{-1}(A)(B) - 2\,k_2(A)^2 + 2\,k_{-2}(AA) = 0 \tag{8}$$

Assuming that rate constants for radical recombination reactions are essentially equal and setting these equal to $k_c$:

$$k_{-1} = k_2 = k_3 \equiv k_c \tag{9}$$

from 8, 9:

$$k_c(A)(B) + 2\,k_c(A)^2 = k_1(AB) + 2\,k_{-2}(AA) \tag{10}$$

We define constants $K$ and $r$:

$$K = k_1/k_{-2}\;k_1k_2/k_{-1}k_{-2} \tag{11}$$

$$k_1 = k_{-2}K$$

$$r = (\mathrm{B})/(\mathrm{A}) \tag{12}$$

$$K = [(\mathrm{AA})_e/(\mathrm{AB})_e]r \tag{13}$$

from 10:

$$k_c(\mathrm{A})^2(2 + r) = k_{-2}K(\mathrm{AB}) + 2\,k_{-2}(\mathrm{AA}) \tag{14}$$

from the stoichiometry:

$$(\mathrm{AB}) = (\mathrm{AB})_i - [(\mathrm{AA}) + (\mathrm{BB})] \tag{15}$$

$$(\mathrm{AB}) = (\mathrm{AB})_i - 2\,(\mathrm{AA}) \tag{16}$$

where $(\mathrm{AB})_i$ is the initial concentration of II.

from 13:

$$k_c(\mathrm{A})^2(2 + r) = k_{-2}K[(\mathrm{AB})_i - 2\,(\mathrm{AA})] + 2\,k_{-2}(\mathrm{AA}) \tag{17}$$

$$(\mathrm{A})^2 = \{k_{-2}K[(\mathrm{AB})_i - 2\,(\mathrm{AA})] + 2\,k_{-2}(\mathrm{AA})\}/(2 + r)k_c \tag{18}$$

from 6:

$$\mathrm{d}(\mathrm{AA})/\mathrm{d}t = k_2(\mathrm{A})^2 - k_{-2}(\mathrm{AA}) \tag{19}$$

$$= k_c(\mathrm{A})^2 - k_{-2}(\mathrm{AA}) \tag{20}$$

$$= \{\{k_{-2}K[(\mathrm{AB})_i - 2(\mathrm{AA})] + 2\,k_{-2}(\mathrm{AA})\}/(2 + r\} - k_{-2}(\mathrm{AA}) \tag{21}$$

$$= k_{-2}\{K[(\mathrm{AB})_i - 2(\mathrm{AA})] + 2(\mathrm{AA}) - (2 + r)(\mathrm{AA})\}/(2 + r) \tag{22}$$

$$= k_{-2}[K(\mathrm{AB})_i - (\mathrm{AA})(2\,K + r)]/(2 + r) \tag{23}$$

$$(2 + r)\int \mathrm{d}(\mathrm{AA})/[K(\mathrm{AB})_i - (\mathrm{AA})(2\,K + r)] = \int k_{-2}\mathrm{d}t \tag{24}$$

$$k_{-2}t = [-(2 + r)/(2\,K + r)]\ln[K(\mathrm{AB})_i - (\mathrm{AA})(2\,K + r)] + [(2 + r)/(2\,K + r)]\ln K(\mathrm{AB})_i \tag{25}$$

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